ADDITIVITY RULES FOR THE ESTIMATION OF THERMOCHEMICAL PROPERTIES[1a]

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Received April 24, 1968

Contents

I. Introduction

The purpose of this review is to extend, as a result of the large increase in data since 1958, the group additivity scheme for estimation of thermochemical properties as originally proposed by Benson and Buss[2] (BB). Because the principal interest of the authors is the application of thermochemistry to chemical kinetics, $C_p°$ contributions have been tabulated as a function of temperature and all values predicted from the group tables refer to the gas phase. The original concept has been expanded to include cyclic compounds and, whenever possible, the experimental data are critically reviewed up to December of 1967. Sufficient data are available for hydrocarbons to render suspect any data which deviate from the value predicted by the scheme, by more than 1 cal/(mole deg) in $C_p°$ or $S°$, or 1 kcal/mole in $\Delta H_f°$. Somewhat larger errors in experimental values may therefore be detected by comparison with predicted values. From the tables of experimental data, it is clear that there are many common compounds for which the values of heat capacity and entropy are unmeasured.

In the interests of accuracy, most weight has been given to data produced after 1930, but the accuracy of thermochemical data is not uniform over all classes of compounds, and the reader is referred to the text on the appropriate compound type for a critical appraisal of the associated errors. Sources of inaccuracy in heats of formation are the inherent error in the use of heats of combustion, which are typically about ±1 kcal/mole, the neglect by many authors of the change in latent heat of vaporization with temperature, and the necessity of estimating unmeasured latent heats. This last is smaller than the first two sources, the formula used in this review having been found to give satisfactory results. It is $\Delta H_{\text{vap}(25°)} = S_{\text{T}}[(1.76 \times 10^{-3})t_{\text{B}} + 0.253]$, where $\Delta H_{\text{vap}(25°)}$ is in kilocalories/mole, S_{T} is the Trouton constant, usually 22 cal/(mole deg); and t_{B}, the boiling point, is in degrees centigrade. Entropies and heat capacities are determined either calorimetrically or from vibrational assignment and statistical formulas. In the former case, errors are likely to be quite small, and in the latter case errors depend on the accuracy of the assignment, especially of the lower frequency modes, and often on the suitability of estimated barriers to internal rotation.

II. General Discussion

The reader is referred to BB[2] for an extensive discussion of additivity rules and the hierarchy of approximations which exist. It is sufficient for the purposes of the present review to remind the reader of the basic concept and the assumptions involved.

For the disproportionation reaction

$$\text{RNN'R} + \text{SNN'S} \rightleftarrows \text{RNN'S} + \text{SNN'R}$$

the group additivity law assumes that $\Delta\Phi = \Delta\Phi_\sigma$, where Φ is any molecular property and $\Delta\Phi_\sigma$ is the contribution to that property due to symmetry changes and optical isomerism.

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[1] (a) This work has been supported in part by Grant No. AP-00353-03 from the Department of Air Pollution, Public Health Service. (b) University of Strathclyde, Glasgow C1, U. K. (c) San Diego State College, Department of Chemistry, San Diego, Calif. (d) Texas A & M University, Department of Chemistry, College Station, Texas. (e) The University, Department of Chemistry, Whiteknights Park, Reading, Berkshire, England.

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

Table I[a]

Alkanes

(C–(C)(H)$_3$; C–(C)$_2$(H)$_2$; C–(C)$_3$(H); C–(C)$_4$; Alkane *gauche* Correction)

	$\Delta H_f°$				$S°$			$C_p°_{300}$[c]			$C_p°_{800}$		
	Obsd	*Estd*	Δ[b]	σ	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ
Ethane	−20.24	−20.16	−0.08	2×3^2	54.85	55.09	−0.2	12.65	12.38	0.3	25.83	26.04	−0.2
Propane	−24.82	−25.11	0.29	2×3^2	64.51	64.51	0.0	17.66	17.88	−0.2	37.08	37.11	0.0
n-Butane	−30.15	−30.06	−0.09	2×3^2	74.12	73.93	0.2	23.40*	23.38	0.0	48.23	48.19	0.0
n-Hexane	−39.96	−39.96	0.00	2×3^2	92.83	92.77	0.1	34.37*	34.37	0.0	70.36	70.34	0.0
n-Octane	−49.82	−49.86	0.04	2×3^2	111.55	111.61	−0.1	43.35*	45.36	0.0	92.50	92.48	0.0
n-Decane	−59.67	−59.76	0.09	2×3^2	(130.17)	130.45	−0.3	(56.34)	56.35	0.0	(114.63)	114.63	0.0
n-Dodecane	−69.52	−69.66	0.14	2×3^2	(148.78)	149.29	−0.5	(67.33)	67.34	0.0	(136.76)	136.78	0.0
2-Methylpropane	−32.15	−32.14	−0.01	3^4	70.42	70.44	0.0	23.25*	23.11	0.1	48.49	48.37	0.1
2-Methylbutane	−36.92	−36.29	−0.63	3^3	82.12	82.04	0.1	28.54*	28.61	−0.1	59.71	59.45	0.3
2,2-Dimethylpropane	−39.67	−39.82	0.15	$3^5 \times 2^2$	72.23	72.88	−0.7	29.21*	29.14	0.1	60.78	60.85	−0.1
2,3-Dimethylbutane	−42.49	−42.52	0.03	3^4	87.42	87.39	0.0	33.76	33.84	0.1	70.7	70.70	0.0
2,2,3-Trimethylbutane	−48.96	−48.60	−0.36	3^6	91.61	91.70	−0.1	39.54*	39.86	−0.3	82.73	85.18	−0.5
2,2,3,3-Tetramethylbutane	−53.99	−54.68	0.69	$3^8 \times 2$	93.06	93.45	−0.4	46.29*	45.89	0.4	96.18	95.66	−0.5

[a] Data from API compilation, except when noted. [b] Alkane group values for $\Delta H_f°$ and $S°$ are from ref 2. [c] Data marked with an asterisk used in a regression coefficient analysis to obtain the group values.

For the molecular properties of interest here, $\Delta H_T \rightarrow 0$, $\Delta C_p°_T \rightarrow 0$, and $\Delta S_T \rightarrow \Delta S_\sigma = R \ln K_\sigma$, where $K_\sigma = \sigma(\text{RNN'R})\sigma(\text{SNN'S})/\sigma(\text{RNN'S})\sigma(\text{SNN'R})$, σ(x) being the symmetry number including both internal and external symmetry. An additional term for entropy of mixing, due to the existence of optical isomers, will be discussed below.

If the molecular framework NN′ is two atoms or greater, these relationships imply the additivity of group properties, which include all nearest neighbor interactions, since a group is defined as an atom together with its ligands (*e.g.*, in the group C–(H)$_3$(C) the central C atom is bonded to three H atoms and one C atom). Thus the equation

$$CH_3OH + CH_3CH_2OCH_3 \rightleftharpoons CH_3CH_2OH + CH_3OCH_3$$

implies the additivity of the properties of the groups C–(H)$_3$(C), C–(H)$_3$(O), O–(C)(H):, C–(H)$_2$(C)(O), and O–(C)$_2$, if the appropriate $\Delta\Phi = \Delta\Phi_\sigma$.

Several groups can be uniquely determined from simple molecules with well-known properties, but there are some groups which exist only in conjugate pairs, either as sums or differences. In this latter case, we have arbitrarily assigned values to one of the pairs. This was not done previously but greatly facilitates calculations without affecting the value of any property of any molecule.[3]

The basic approximation of group additivity makes no allowance for next-nearest neighbor interactions, but there are some molecules in which such interactions have considerable influence on the molecular properties. Such refinements are tabulated in the present scheme under the label of conformational corrections. The group values in the tables are based on the most stable conformation.

Since all carbon–carbon double bonds are between two sp^2 carbon atoms, the nomenclature C$_d$–(H)$_2$ is used to replace the former, C$_d$–(C$_d$)(H)$_2$, etc. Similar treatment is given to triple bonds, C$_t$–(X), aromatic ring carbon atoms, C$_B$–(X), and C$_a$, the allenic group >C=C=C<. Other group abbreviations are noted at the end of the appropriate table.

Arbitrarily assigned group values are indicated by placing the group name in square brackets. Individual values which have been estimated are in parentheses. Values of Δ, which is defined as the difference between observed and estimated values, are quoted as [0] when the compound in question is the sole basis for a particular group. Entropies and heat capacities calculated from spectroscopically determined vibrational frequencies are here considered as measured, even if internal rotation barriers were transferred from another molecule. All original references are given where possible with the exception of values obtained from the American Petroleum Institute compilation, "Selected Values of Physical and Thermochemical Properties of Hydrocarbons and Related Compounds," by F. D. Rossini, *et al.*, Carnegie Press, Pittsburgh, Pa., 1953, which is the source of all unreferenced entries. If any entry comes from more than one source, one of which is the above, it is referenced as A.

Recognizing that their search for data, while it was exhausting, may not have been exhaustive, the authors would be grateful to have any values of thermodynamic properties of the type listed here brought to their notice. When sufficient such numbers are available, we will issue a set of revised tables.

III. Hydrocarbons

A. ALKANES (C-(C)(H)$_3$; C-(C)$_2$(H)$_2$; C-(C)$_3$(H); C-(C)$_4$, ALKANE *gauche*)

The values of the group contribution to heat of formation and entropy were taken directly from BB,[2] as was the value for the *gauche* correction. Values for the heat capacity, obtained from a multiple linear regression coefficient analysis (MLRCA), are listed in Table I.

Corrections to the heat of formation for *gauche* configurations are made one for each such conformation in a molecule. Thus, observing along a C(sp^3)–C(sp^3) bond, as shown in Figure 1, the *gauche* corrections are as listed for the substituted butanes.

Analysis of the simply branched alkanes will show deviations predominantly small and of the same sign, *i.e.*, $\Delta H_{\text{obsd}} - \Delta H_{\text{estd}} \sim 0.4$ kcal/mole. This is done deliberately to avoid

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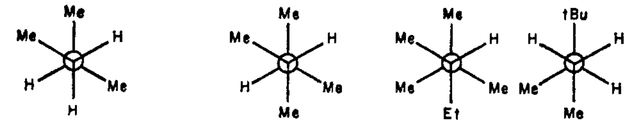
(3) This represents a change of policy; see ref 42 in ref 2.



1 GAUCHE CORRECTION;
2 METHYLBUTANE

2 GAUCHE CORRECTIONS;
2,3 DIMETHYLBUTANE

4 GAUCHE + I GAUCHE
5 GAUCHE CORRECTIONS
2,2,3 TRIMETHYLPENTANE

Figure 1.

Table II

The C_9 Hydrocarbons[a]

Compound	$\Delta H_f°$ *Obsd*	$\Delta H_f°$ *Estd*	Δ
3,3-Diethylpentane	−55.44	−53.22	−2.22
2,2,3,3-Tetramethylpentane	−56.70	−58.03	1.33
2,2,3,4-Tetramethylpentane	−56.64	−58.98	2.34
2,2,4,4-Tetramethylpentane	−57.83	−61.23	3.40
2,3,3,4-Tetramethylpentane	−56.46	−59.00	2.54

[a] Values from A. Labbauf, J. B. Greenshields, and F. D. Rossini, *J. Chem. Eng. Data*, 6, 261 (1961).

excessively large errors in the heavily substituted alkanes. The largest error of +3.4 kcal/mole among the latter occurs with 2,2,4,4-tetramethylpentane. This compound has two *t*-butyl groups on the same atom and six *gauche* interactions. Data from related compounds, such as di-*t*-butyl ether, will show that *gauche* interactions do not account sufficiently for the strain which is between H atoms and C atoms separated by three C atoms, a next-next-next-nearest neighbor interaction. No simple scheme can ever hope to account for such a distant interaction, and these may be expected to occur frequently in heavily branched compounds. Thus the discrepancies shown in Table II are probably real.

B. ALKENES

1. *Monoolefins* (C_d–$(H)_2$; C_d–$(C)(H)$; C_d–$(C)_2$; C–$(C_d)(C)(H)_2$; C–$(C_d)(C)_2(H)$; C–$(C_d)(C)_3$; alkene *gauche*; *cis* correction)

As can be seen from Table III,[4–13] there is a comparatively large number of values of the heats of formation of this class of compounds. Group contributions to the heat of formation were arrived at by subtracting all alkane group and *gauche* contributions and obtaining a MLRCA for the molecules indicated in the table. (The *cis* interaction was fixed at 1.00 kcal/mole, except when one of the interacting groups is a *t*-butyl, in which case the *cis* correction is 4.00 kcal/mole, or when a molecule has two *cis* interactions, such as 2,3-dimethylbut-2-ene, where the total *cis* correction is 3.00 kcal/mole.)

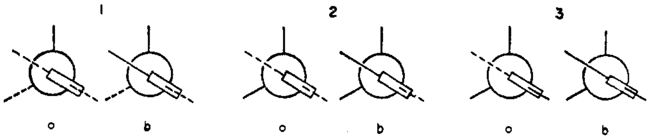


Figure 2.

The available data for entropy and heat capacity are considerably less than for the heats, but sufficient measured values exist to determine the group contributions from the MLRCA fit of the data so marked in the table.

The question of *gauche* interactions along a $C(sp^3)$–$C(sp^2)$ bond has been taken into account, as indicated in Figure 2. In this figure (1a, 2a, and 3a) is depicted the supposed most stable conformations when the sp^3 carbon has a hydrogen substituent (indicated by dashed line), as the sp^3 carbon increases in substitution from one to three heavy groups (indicated by full lines). It seems clear that in cases 1a and 2a no significant interaction need arise. In case 3a, while significant interaction may be expected, it will always be taken into account by the group C–$C_d(C)_3$, which always implies the presence of the second sp^2 carbon, which is interacting with the heavy substituents on the sp^3 carbon.

Figure 2 (1b, 2b, and 3b) depicts what are supposed to be the most stable conformations with heavy substituents on the central sp^2 carbon (1a, 2a, and 3a). It is seen that in 1b, we might expect to have one alkene *gauche* correction, while molecules of the class of 2b and 3b have two alkene *gauche* corrections.

Comparing the C–C distances of the interacting groups in the alkene and in the alkane cases, about 3.2 Å in the former and 2.8 Å in the latter, we expect a smaller effect. In fact, the effect is small enough that we have chosen to ignore it in cases of the type 1b (*i.e.*, one *gauche*) and to make a correction only in cases 2b and 3b. The correction in Table XXXIII is this total correction.

Entropy and heat capacity have been determined from a MLRCA fit of the indicated data. The *cis* correction to the entropy in entropy units is +1.2 for but-2-ene, 0 for all other 2-ene's, and −0.6 for 3-ene's.

There are no measured data to lead to entropy and heat capacity values for the groups C–$(C_d)(C)_2(H)$ and C–$(C_d)(C)_3$. The group values have been estimated as shown in the footnotes of Table III. These estimates lead to significantly different values than do the incremental estimates of the API original reference. These are first encountered in 3-methylbut-1-ene and 3,3-dimethylbut-1-ene, respectively. (Entropy and heat capacity values in API, other than those tabulated here, are all estimated.)

2. *Dienes* (C_a; C_d–$(C_d)(H)$; C_d–$(C_d)(C)$; C–$(C_d)_2(H)_2$)

These molecules with allenic double bonds can be fitted to group values by the introduction of the C_a group, which accounts for the properties of $>C{=}C{=}C<$. The end carbon atoms are treated as normal C_d's. As can be seen from Table III, this accounts quite well for both the measured data and the incremental estimates in API with a mild exception in the heat capacity values of 1,2-pentadiene.

For the nonallenic dienes, there are enough data to get a value for all group contributions to the heat of formation, but the contributions of the group C–$(C_d)_2(H)_2$ to the entropy

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(4) H. F. Bartolo and F. D. Rossini, *J. Phys. Chem.*, **64**, 1686 (1960).
(5) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 504 (1967).
(6) D. M. Golden, *et al.*, *ibid.*, **86**, 5416 (1964).
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(10) J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).
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(12) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 3311 (1965).
(13) N. P. Bekkedahl and L. A. Wood, *J. Res. Natl. Bur. Std.*, **19**, 55 (1937).

Table III[a]

Alkenes

	ΔH_f°						S°				$C_p{}^\circ{}_{300}$			$C_p{}^\circ{}_{800}$			
	Obsd	*Estd*	Δ	*Ref*	*n*	*σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Monoolefins: $C_d-(H)_2$; $C_d-(C)(H)$; $C_d-(C)_2$; $C-(C_d)(C)(H)_2$; $C-(C_d)(C)_2(H)$; $C-(C_d)(C)_3$; *cis* Correction; Alkene *gauche*																	
Ethene	12.50*	12.22	0.28			2^2	52.45	52.46	0.0		10.45*	10.21	0.2	20.20	20.13	0.1	
Propene	4.88*	4.78	0.10			3	63.80*	63.72	0.1		15.34*	15.45	−0.1	30.68	31.73	0.0	
But-l-ene	− 0.03*	− .01	−0.04			3	73.80*	73.52	0.3	A, 6, 7	20.57	20.58	0.0	41.80	41.65	0.2	
cis-But-2-ene	− 1.67*	− 1.97	0.30			$3^2 \times 2$	72.10*	72.08	0.0	A, 6, 7	18.96*	19.36	−0.4	40.87	40.94	0.1	
trans-But-2-ene	− 2.67*	− 2.97	0.30			$3^2 \times 2$	70.86*	70.88	0.0	A, 6, 7	21.08*	20.70	0.4	41.50	41.33	0.2	
2-Methylpropene	− 4.04*	− 3.56	−0.48			$3^2 \times 2$	70.17	70.37	−0.2		21.39*	21.57	−0.2	41.86	41.91	0.1	
Pent-1-ene	− 5.00*	− 4.96	−0.06			3	83.25*	83.32	−0.1	A, 7, 8	26.31	26.07	0.2	52.95	52.72	0.2	
cis-Pent-2-ene	− 6.71*	− 6.73	0.02			3^2	81.56*	82.15	−0.6	A, 7	(24.45)	24.49	0.0	(52.29)	52.16	0.1	
trans-Pent-2-ene	− 7.59*	− 7.73	0.14			3^2	81.96*	82.15	−0.2	A, 7	(26.04)	25.82	0.2	(52.45)	52.55	−0.1	
2-Methylbut-1-ene	− 8.68*	− 8.32	−0.36			3^2	81.15*	81.15	[0]	9	26.41*	26.70	−0.3	53.15	53.13	0.0	9
3-Methylbut-1-ene	− 6.92*	− 6.78	−0.14			3^2	(79.70)[b]	80.35	−0.7		(28.47)[b]	25.88	2.6	(53.85)[b]	53.23	−0.6	
2-Methylbut-2-ene	−10.17*	−10.30	0.13			3^2	80.92	81.06	−0.1		25.22*	25.49	−0.3	52.05	52.11	0.1	
Hex-1-ene	− 9.96*	− 9.88	−0.08														
cis-Hex-2-ene	−12.51*	−11.68	0.83	4													
trans-Hex-2-ene	−12.88*	−12.68	−0.20	4													
cis-Hex-3-ene	−11.38*	−11.49	0.11	4													
trans-Hex-3-ene	−13.01*	−12.49	−0.52	4													
2-Methylpent-1-ene	−14.19*	−13.27	−0.92	4													
3-Methylpent-1-ene	−11.82*	−11.73	−0.09	4													
4-Methylpent-1-ene	−12.24*	−11.17	−1.07	4													
2-Methylpent-2-ene	−15.98*	−15.06	0.92	4													
3-Methyl-*cis*-pent-2-ene	−14.86*	−15.06	0.20	4													
3-Methyl-*trans*-pent-2-ene	−15.08*	−15.06	−0.02	4													
4-Methyl-*cis*-pent-2-ene	−13.73*	−13.53	−0.20	4													
4-Methyl-*trans*-pent-2-ene	−14.69*	−44.53	−0.16	4													
2-Ethylbut-1-ene	−13.38*	−13.18	−0.20	4													
2, 3-Dimethylbut-1-ene	−15.85*	14.65	−1.20	4													
3, 3-Dimethylbut-1-ene	−14.70*	−13.71	−0.99	4		3^4	(82.16)[c]	80.95	1.2		(30.39)[c]	31.82	−1.4	(63.6)[c]	65.7	−2.1	
2, 3 Dimethylbut-2-ene	−16.68	−16.74	0.06	4													
Hept-1-ene	−14.89*	−14.84	−0.05														
trans-Hept-2-ene	−17.6	−17.6	0.0	5													
cis-Hept-2-ene	−16.9	−16.6	−0.3	5													
trans-Hept-3-ene	−17.6	−17.4	−0.2	5													
cis-Hept-3-ene	−16.9	−16.4	−0.5	5													
3-Methyl-*cis*-hex-3-ene	−19.22*	−19.83	0.61	10													
3-Methyl-*trans*-hex-3-ene	−18.60*	−19.83	1.23	10													
2, 4-Dimethylpent-1-ene	−20.27*	−19.50	−0.77	10													
4, 4-Dimethylpent-1-ene	−19.20*	−18.17	−1.13	10													
2,4-Dimethylpent-2-ene	−21.44	−21.40	−0.04	10													
4,4-Dimethyl-*cis*-pent-2-ene	−17.60*	−17.46	−0.14	10													
4,4-Dimethyl-*trans*-pent-2-ene	−21.46*	−21.47	0.01	10													
3-Methyl-2-ethylbut-1-ene	−19.25*	−19.41	0.16	10													
2,3,3-Trimethylbut-1-ene	−20.67	−20.94	0.27	10													

Oct-1-ene	−19.82*	−20.14	0.32													
2,2-Dimethyl-*cis*-hex-3-ene	−21.77*	−22.23	0.46	10												
2,2-Dimethyl-*trans*-hex-3-ene	−26.16*	−26.23	0.07	10												
2-Methyl-3-ethylpent-1-ene	−24.40*	−24.55	0.15	10												
2,4,4-Trimethylpent-1-ene	−26.68*	−26.38	−0.30	10												
2,4,4-Trimethylpent-2-ene	−25.50*	−25.80	0.30	10												
Allenic Dienes: C_a																
Allene	45.92*	46.72	−0.80		2^2	58.30*	58.7	−0.4		14.16*	14.1	0.1	25.42*	25.4	0.0	
1,2-Butadiene	38.77*	38.97	−0.20	A, 11	3	70.03*	70.0	0.0		19.23*	19.4	−0.2	36.01*	36.0	0.0	
1,2-Pentadiene	33.61*	34.21	−0.60	11	3	(79.7)	79.8	−0.1		(25.3)	24.5	0.8	(47.7)	47.4	0.3	*g*
2,3-Pentadiene	31.79*	31.12	0.57	11	2 $3^2 \times 2$	(79.0)	78.6	0.4		(24.3)	24.6	−0.3	(46.6)	46.6	0.0	
3-Methyl-1,2-butadiene	(31.00)	30.64	0.36		2×3^2	(76.4)	76.2	0.2		(25.3)	25.5	−0.2	(47.2)	47.2	0.0	
Nonallenic Dienes: $C_d{-}(C_d)(H)$; $C_d{-}(C_d)(C)$; $C{-}(C_d)_2(H)_2$																
1,3-Butadiene	26.33*	26.48	−0.15		2	66.62	66.6	[0]		19.11	19.1	[0]	36.84	36.8	[0]	
cis-1,3-Pentadiene	19.77*	19.73	0.04	11, 12	3	(76.5)	76.5	0.0	A, 12	(22.7)	23.0	−0.3	(47.0)	47.2	−0.2	
trans-1,3-Pentadiene	18.77*	18.73	0.04	11, 12	3	(76.4)	76.5	−0.1	A, 12	(24.9)	24.4	0.5	(47.7)	47.6	0.1	
1,4-Pentadiene	25.41	25.41	[0]	11	2	(79.7)[d]	80.0	−0.3		(25.2)[d]	23.2	2.0	(47.6)[d]	46.7	0.9	
2-Methyl-1,3 butadiene (isoprene)	18.09	18.09	[0]	11	3	75.2	75.2	[0]	13	(25.2)[e]	24.8	0.4	(48.0)[e]	47.2	0.8	

[a] Starred values used in regression coefficient analysis to obtain group values. [b] $C{-}(C_d)(C)_2(H) = C{-}(C)_3(H) + [C{-}(C_d)(C)(H)_2{-}C{-}(C)_2(H)_2]$. [c] $C{-}(C_d)(C)_3 = C{-}(C)_4 + [C{-}(C_d)(C)(H)_2{-}C{-}(C)_2(H)_2]$. [d] $C{-}(C_d)_2(H)_2 = C{-}(C_d)(C)(H)_2 + [C{-}(C_d)(C)(H)_2 - C{-}(C)_2(H)_2]$. [e] $C_d{-}(C_d)(C) = C_d{-}(C)_2 + [C_d{-}(C_d)(H) - C_d{-}(C)(H)]$. [f] The value in API has been raised by $R \ln 2$ to take into account the effect of optical isomers which was neglected in the original reference: J. Kilpatrick, *et al.*, *J. Res. Natl. Bur. Std.*, **42**, 225 (1949). [g] Group values preferred, as quoted values differ from other allenic molecules by relatively large amounts.

and heat capacity, and that of the group $C_d{-}(C_d)(C)$ to heaf capacity, had to be estimated as indicated in the footnotes ot Table III. These estimates lead to heat capacity values which are somewhat at variance with the estimates in the API tables.

C. ALKYNES ($C_t{-}(H)$; $C_t{-}(C)$; $C{-}(C_t)(C)(H)_2$; $C{-}(C_t)(C)_2(H)$; $C_t{-}(C_d)$; $C_d{-}(C_t)(H)$)

The contributions of the first four groups mentioned above to heat of formation can be obtained from the data in the API tables in the usual manner. The entropy and heat capacity contributions of all but $C{-}(C_t)(C)_2(H)$ can also be ascertained from measured values, the contributions of this group being determined as noted in Table IV.[14]

From some observed values of heats of formation of some mixed "yne–ene" compounds, based on solution heats of hydrogenation, one can ascertain the heat of formation contribution of the sum of groups $C_t{-}(C_d) + C_d{-}(C_t)(H)$. We have arbitrarily assigned to the $C_d{-}(C_t)(H)$ group the same values as the $C_d{-}(C_d)(H)$ group, and thus obtained values for the $C_t{-}(C_d)$ group.

D. AROMATICS (TABLE V)

1. *Alkylbenzenes* ($C_B{-}(H)$; $C_B{-}(C)$; $C{-}(C_B)(C)(H)_2$; $C{-}(C_B)(C)_2(H)$; $C{-}(C_B)(C)_3$; *ortho* correction)

Values were obtained in a straightforward manner from those values so marked. Where group values were estimated, the nature of the estimation is noted.

2. *Unsaturated Benzenes* ($C_B{-}(C_d)$; $C_d{-}(C_B)(H)$; $C_d{-}(C_B)(C)$; $C_B{-}(C_t)$; $C_t{-}(C_B)$)

There seems to be very little in the way of measured values for this class of compounds. The contributions of the sum of the $C_B{-}(C_d)$ and $C_d{-}(C_B)(H)$ groups can be obtained from styrene itself, and this value allows the estimation of the properties of the other vinylbenzenes listed, with the exception of α-methylstyrene. For convenience, the $C_d{-}(C_B)(H)$ group is arbitrarily assigned the values of the $C_d{-}(C_d)(H)$ group. The measured value of the heat of formation of α-methylstyrene yields values for the $C_d{-}(C_B)(C)$ group contribution. The entropy and heat capacity contributions of this group are estimated as equal to those of the $C_d{-}(C_d)(C)$ group.

The values of entropy and heat capacity contributions of the sum $[C_B{-}(C_t) + C_t{-}(C_B)]$ are estimated from phenylacetylene, and the $C_B{-}(C_t)$ group is assigned the values of the $C_B{-}(C_d)$ group. The heat of formation is estimated as shown in Table V.[15–19]

E. POLYAROMATICS (TABLE VI[20–22])

The measured values for biphenyl yield the contributions of the group $C_B{-}(C_B)$ in a straightforward manner. This group seems to reproduce the heats of naphthalenic compounds

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Table IV[a]

Alkynes

(C$_t$–(H); C$_t$–(C); C–(C$_t$)(C)(H)$_2$; C–(C$_t$)(C)$_2$(H); C$_t$–(C$_d$); C$_d$–(C$_t$)(H))

	ΔH_f°					S°				$C_p^{\circ}{}_{300}$			$C_p^{\circ}{}_{800}$			
	Obsd	*Estd*	Δ	*Ref*	σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Ethyne	54.19*	53.86	0.33		2	48.00*	48.0	0.0		10.53	10.54	0.0	14.93	14.9	0.0	
Propyne	44.32*	44.40	−0.08		3	59.30*	59.3	0.0		14.55	14.6	0.0	25.14	25.1	0.0	
But-1-yne	39.48*	39.67	−0.19		3	69.51*	69.6	−0.1		19.54	19.5	0.0	35.95	36.0	0.0	
But-2-yne	34.97*	34.94	0.03		$3^2 \times 2$	67.71*	67.8	−0.1		18.70	18.6	0.0	35.14	35.2	−0.1	
Pent-1-yne	34.50*	34.72	−0.22		3	(79.10)	79.0	0.1		(25.65)	25.0	0.7	(47.1)	47.0	0.1	
Pent-2-yne	30.80*	30.21	0.59		3^2	(79.30)	79.5	−0.2		(23.69)	23.6	0.1	(45.9)	46.1	−0.2	
3-Methylbut-1-yne	32.60*	32.60	[0]		3^2	(76.23)^{b}	76.2	0.0		(25.1)^{b}	24.8	0.3	(47.4)^{b}	47.2	0.2	
Hexa-1,5-diyne (dipropargyl)	99.44*	99.50	−0.06	14^{c}												
cis-Pent-3-en-1-yne	60.60*	61.64	−1.04	14^{c}												
trans-Pent-3-en-1-yne	60.92*	60.64	0.28	14^{c}												
cis-Dec-3-en-1-yne	36.25	36.81	−0.56	14^{c}												
trans-Dec-3-en-1-yne	36.95*	35.91	1.04	14^{c}												

[a] Starred values used in regression coefficient analysis to obtain group values. [b] C–(C$_t$)(C)$_2$(H) = C–(C)$_3$(H) + [C–(C$_t$)(C)(H)$_2$–C–(C)$_2$(H)$_2$]. [c] These are calculated from heats of hydrogenation tudies in solution which are often low by 1 or 2 kcal/mole.

Table V

Aromatics

	ΔH_f°					S°				$C_p^{\circ}{}_{300}$			$C_p^{\circ}{}_{800}$			
	Obsd	*Estd*	Δ	*Rej*	σ	*Obsd*	*Estd*	Δ	*Rej*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Rfe*
Alkylbenzenes: (C$_B$–(H); C$_B$–(C); C–(C$_B$)(C)(H)$_2$; C–(C$_B$)(C)$_2$(H); C–(C$_B$)(C)$_3$; *ortho* Correction)																
Benzene	19.82	19.79	0.03		3×2^2	64.34*	64.26	0.1		19.65*	19.42	0.2	45.06*	45.21	−0.2	
Toluene	11.95*	11.92	0.03		3×2	76.64*	76.81	−0.2	17	24.94*	25.04	-0.1	56.61*	55.66	1.0	17
Ethylbenzene	7.12*	7.06	0.06		3×2	86.15*	86.15	[0]		30.88*	30.88	[0]	67.15*	67.15	[0]	
Isobutylbenzene	−5.15	−4.92	−0.23	15	$3^2 \times 2$	...	102.33	...	..	...	41.61	..	..	89.48	..	..
1,2-Dimethylbenzene	4.54*	4.63	−0.09		$3^2 \times 2$	84.34*	84.21	0.1	16	32.10*	31.79	0.3	66.50*	66.98	−0.5	16
1,3-Dimethylbenzene	4.12*	4.06	0.06		$3^2 \times 2$	85.49*	85.82	−0.3		30.66*	30.66	0.0	66.41*	66.10	0.3	
1,4-Dimethylbenzene	4.29*	4.06	0.23		$3^2 \times 2$	84.23*	84.45	−0.2		30.49*	30.66	−0.2	66.14*	66.10	0.0	
n-Propylbenzene	1.87*	2.11	−0.24		3×2	(95.74)	95.59	0.2		(36.99)	36.48	0.5	(78.30)	78.22	0.1	
n-Butylbenzene	−3.30*	−2.84	−0.46		3×2	(105.04)	105.01	0.0		(42.09)	41.98	0.1	(89.37)	89.29	0.1	
1-Propylbenzene	0.94*	0.86	0.08		$3^2 \times 2$	(92.87)^{a}	92.91	0.0		(36.47)^{a}	36.11	0.4	(78.6)^{a}	78.41	0.2	
sec-Butylbenzene	−4.17*	−4.09	−0.08	15	$3^2 \times 2$	...^{a}	102.33	...	..	...^{a}	41.61	...	...^{a}	89.48	...	..
t-Butylbenzene	−5.42*	−5.42	[0]	15	$3^4 \times 2$	...^{b}	95.93	...	..	...^{b}	42.13	...	...^{b}	90.89	...	..
1-Methyl-2-ethylbenzene	0.29*	−0.23	0.52		3^2	(95.42)	94.93	0.5		(37.94)	37.63	0.3	(78.1)	78.47	−0.4	

quite well, but begins to fall off with larger compounds of this class. While the value for anthracene is not bad, it is clear from the value of phenanthrene that this type of pseudo group additivity does not take into account some important interactions. Note that biphenyl is not planar in the gas phase so that it may be lacking in some conjugation energy. The value shown for $\Delta H_f°(C_B–C_B)$ was an average over biphenyl and naphthalenes.

Entropy and heat capacity can be treated with a ring correction, as for the cycloalkanes and alkenes treated in the next section.

F. CYCLIC ALKANES AND ALKENES

Our approach to cyclic compounds has been to use groups from the open-chain compounds and a ring correction. In the case of heats of formation, this correction is what is often defined as the strain energy. Since the available data are sparse, all ring strains were evaluated from the unsubstituted rings where data for these were available. (For the cyclohexanes, enough data are available to allow us to relax this rule.) The transferability of this strain to substituted ring compounds is generally attested to by the data of Table VII.[23–51] It will be noticed that the deviations are somewhat larger than previously encountered. This is due to the absence of gas-phase data, the use of the unsubstituted ring as standard, and perhaps small differences in the strain energies of various substituted small rings.

The entropy and heat capacity correction terms are also seen to be transferable. Again, an examination of the deviations will show that choice of the unsubstituted ring as the standard often throws the values of the substituted compounds off by a small amount.

The magnitude of the entropy corrections is not surprising when one realizes that a disproportionate amount of the entropy is tied up in the C–(H)$_3$(C) and C$_d$–(H)$_2$ groups of open-chain molecules.

1-Methyl-3-ethylbenzene	−0.46	−0.80	0.34		3^2	(96.60)	96.54	0.1		(36.59)	36.51	0.1	(77.8)	77.59	0.2	
1-Methyl-4-ethylbenzene	−0.78	−0.80	0.02		$3^2 \times 2$	(95.34)	95.18	0.2		(36.42)	36.51	−0.1	(77.6)	77.59	0.0	
1,2,3-Trimethylbenzene	−2.29*	−2.66	0.37		$3^3 \times 2$	91.79*	91.60	0.2	16	37.82*	38.53	−0.7	77.56*	78.30	−0.7	16
1,2,4-Trimethylbenzene	−3.33*	−3.24	−0.09		3^3	94.54*	94.58	0.0	16	36.99*	37.41	−0.4	76.93*	77.41	−0.5	16
1,3,5-Trimethylbenzene	−3.84*	−3.81	−0.03		$3^4 \times 2$	92.15*	92.65	−0.5		36.10*	36.29	−0.2	76.84*	76.51	0.3	
1,2,3,4-Tetramethylbenzene	−10.02*	−9.96	−0.06		$3^4 \times 2$	99.55*	99.00	0.6	16	45.50*	45.28	0.2	89.42*	89.62	−0.2	16
1,2,3,5-Tetramethylbenzene	−10.71*	−10.54	−0.17		$3^4 \times 2$	100.99*	100.62	0.4	16	44.57*	44.16	0.4	88.79*	88.74	0.1	16
1,2,4,5-Tetramethylbenzene	−10.82*	−10.53	−0.29		$3^4 \times 2^2$	100.03*	99.26	0.8	16	44.77*	44.16	0.6	88.41*	88.74	−0.3	16
Pentamethylbenzene	(−17.79)	−17.27	−0.52	16	$3^5 \times 2$	106.09*	106.40	−0.3	16	51.99*	52.03	0.0	101.29*	100.94	0.4	16
Hexamethylbenzene	(−25.26)	−24.00	−1.26	16	$3^7 \times 2^2$	108.12*	108.65	−0.5	16	59.73*	59.90	−0.2	113.51*	113.14	0.4	16
Bibenzyl	32.41	34.30	−1.9	18	2^2	...	129.90	...	..	...	44.08	...	...	85.98	...	..
Unsaturated Benzenes: $C_B–(C_d)$; $C_d–(C_B)(H)$; $C_d–(C_B)(C)$; $C_B–(C_t)$; $C_t–(C_B)$																
Styrene	35.22	35.22	[0]		2	82.48	82.48	[0]		29.35	29.35	[0]	61.40	61.40	[0]	
S-Methylstyrene	27.00	27.00	[0]		3×2	(91.7)[c]	89.73	2.0		(34.9)[c]	35.48	−0.6	(71.8)[c]	72.57	−0.8	
cis-β-Methylstyrene	(29.00)	28.77	0.23		3×2	(91.7)	91.07	0.6		(34.9)	33.26	0.6	(71.8)	71.61	0.2	
trans-β-Methylstyrene	(28.00)	27.77	0.23		3×2	(90.9)	91.07	0.8		(35.1)	34.60	0.5	(72.2)	72.00	0.2	
o-Methylstyrene	(28.30)	27.92	0.38		3	(91.7)	91.24	0.5		(34.9)	36.09	−1.2	(71.8)	71.82	0.0	
m-Methylstyrene	(27.60)	27.35	0.25		3	(93.1)	92.85	0.3		(34.9)	34.97	−0.1	(71.8)	70.94	0.9	
p-Methylstyrene	(27.40)	27.35	0.05		3×2	(91.7)	91.49	0.2		(34.9)	34.97	−0.1	(71.8)	70.94	0.9	
Ethynylbenzene	...[d]	(78.31)	...		2	76.88	76.88	[0]	19	27.63	27.63	[0]	55.79	55.79	[0]	19

[a] $C–(C_B)(C)_2(H) = C–(C)_3(H) + [C–(C_B)(C)(H)_2 - C–(C)_2(H)_2]$. [b] $C–(C_B)(C)_3 = C–(C)_4 + [C–(C_B)(C)(H)_2 - C–(C)_2(H)_2]$. [c] $C_d–(C_B)(C) = C_d–(C_d)(B)$. [d] $(C_t–(C_B) = C_t–(C_d)$.

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Table VI

	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	*Estd*	Δ	*Ref*	σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Biphenyl	43.52	42.92	0.60	18	2^3	93.91	93.91	[0]	21	39.05	39.05	[0]	86.92	86.92	[0]	21
Naphthalene	36.12	36.32	−0.20	18, 20	2^2	80.5^a	80.5	[0]	22							
1-Methylnaphthalene	27.93	28.43	−0.50	20												
2-Methylnaphthalene	27.75	28.43	−0.6	20												
Anthracene	55.17	52.84	2.67	18												
Phenanthrene	49.46	52.84	−3.38	18												

[a] Naphthalenic ring correction = 8.1 gibbs/mole.

Table VII

Nonaromatic Rings: Ring Corrections

	$\Delta H_f°$						$S°$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	*Estd*	Δ	*Ref*	*n*	σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Cyclopropane	12.74	12.7	[0]	23		3 × 2	56.8	56.8	[0]	34	13.44	13.44	[0]	31.44	31.44	[0]	34
Methylenecyclopropane	48.0	48.0	[0]	*e*													
Cyclopropene	66.6	66.6	[0]	24		2	58.38	58.38	[0]	35							
1-Methylcyclopropene	58.2	58.3	−0.1	*e*													
Cyclobutane	16.4	6.4	[0]	25		2^3	63.43	63.43	[0]	36	17.37	17.37	[0]	42.42	42.42	[0]	36
Cyclobutene	37.5	37.5	0.0	*e*		2	62.98	62.98	[0]	37	16.03	16.03	[0]	32.26	32.26	[0]	37
Methylcyclobutane	...	−0.6	..	..													
1,2-Dimethylcyclobutene	20.8	21.7	−0.9	f^a													
1-Methylcyclobutene	29.1	29.1	[0]	$27^{a,b}$													
1-Methyl-3-methylenecyclobutene	48.3	48.6	−0.3	$28^{a,b}$													
Methylenecyclobutane	30.0	28.0	2.0	27^{a-e}													
1,3-Dimethylenecyclobutane	53.3	51.4	1.9	28^{a-e}													
Cyclopentane	−18.46	−18.46	[0]			10	70.0	70.0	[0]		19.98	19.98	[0]	52.44	52.44	[0]	
Cyclopentene	8.56	8.56	[0]	29		2	69.23	69.23	[0]		18.08	18.08	[0]	45.78	45.78	[0]	
Cyclopentadiene	32.44	32.44	[0]	30													
Methylcyclopentane	−25.50	−25.49	−0.0			3	81.22	81.34	−0.1	38	26.43	25.21	1.2	63.8	63.7	−0.1	38
1-Methylcyclopentene	−1.5	−0.29	−1.2	27^a		3	(78.2)	78.1	0.1		(24.3)	24.2	−0.1	(57.0)	57.1	−0.1	
1-Ethylcyclopentene	−5.8	−5.05	−0.8	27^a													
Methylenecyclopentane	2.4	3.32	−0.9	$27^{a,c}$													
Ethylidenecyclopentane	−4.5	−4.13	−0.4	$27^{a,c}$													
1,1-Dimethylcyclopentane	−33.05	−33.17	0.1			3^2 × 2	(85.87)	85.18	0.69		(32.16)	31.23	0.93	(76.18)	76.20	0.0	
cis-1,2-Dimethylcyclopentane	−30.96	−31.51	0.6			3^2	(87.51)	88.14	−0.63		(32.34)	30.44	1.9	74.98	74.94	1.0	
trans-1,2-Dimethylcyclopentane	−32.67	−32.52	−0.2		2	3^2 × 2	(87.67)	88.14	−0.47		(32.44)	30.44	2.0	(75.84)	74.94	0.9	
cis-1,3-Dimethylcyclopentane	−32.47	−32.52	0.6			3^2	87.54	88.14	−0.6	38	32.72	30.44	2.3	75.68	74.94	0.8	38

trans-1,3-Dimethylcyclopentane	−31.93	−32.52	0.1		2	$3^2 \times 2$	(87.54)	88.14	−0.6		(32.72)	30.44	2.3	(75.68)	74.94	0.8	
Cyclohexane	−29.43	−29.73	0.3			3×2	71.28	71.58	−0.3		25.58	26.58	−1.0	66.76	67.26	−0.5	
Cyclohexene	−0.84	−0.84	[0]	31		2	74.27	74.27	[0]		25.28	25.28	[0]	59.49	59.49	[0]	
1,3-Cyclohexadiene	26.0	26.0	[0]	32													
1,4-Cyclohexadiene	26.3	26.3	[0]	33													
Methylcyclohexane	−36.99	−36.76	−0.2			3	82.06	81.86	0.2		32.51	31.81	0.7	78.74	78.5	0.2	
Ethylcyclohexane	−41.05	−40.91	−0.1			3	91.44	91.28	0.3		38.23	37.31	0.9	90.1	89.6	0.5	
1,1-Dimethylcyclohexane	−43.26	−42.81	−0.5			3^2	87.24	87.12	0.1		(37.2)	37.0	0.2	(90.7)	91.0	−0.3	
cis-1,2-Dimethylcyclohexane	−41.15	−41.39	0.2		2	3^2	89.51	89.96	−0.5		(37.7)	37.0	0.7	(90.1)	89.8	0.3	
trans-1,2-Dimethylcyclohexane	−43.02	−42.99	0.0		2	$3^2 \times 2$	88.65	88.60	0.1		(38.3)	37.0	1.3	(90.5)	89.8	0.7	
cis-1,3-Dimethylcyclohexane	−44.16	−43.79	−0.4			3^2	88.54	88.60	−0.1		(37.9)	37.0	1.9	(90.5)	89.8	0.7	
trans-1,3-Dimethylcyclohexane	−42.20	−42.19	0.0		2	3^2	89.92	89.96	0.0		(37.9)	37.0	0.9	(89.8)	89.8	0.0	
cis-1,4-Dimethylcyclohexane	−42.22	−42.19	0.0			3^2	88.54	88.60	−0.1		(37.9)	37.0	0.9	(89.8)	89.8	0.0	
trans-1,4-Dimethylcyclohexane	−44.12	−43.79	−0.3			$3^2 \times 2$	87.19	87.24	−0.1		(38.0)	37.0	1.0	(90.6)	89.8	0.8	
1-Methylcyclohexene	−10.0	−9.7	−0.3	27[a]													
1-Ethylcyclohexene	−15.0	−14.5	−0.5	27[a]													
Methylenecyclohexane	−7.2	−8.1	0.9	27[a,c]													
Ethylidenecyclohexane	−13.7	−15.5	1.8	27[a,c]													
Cycloheptane	−28.3	−28.3	[0]	25	1		81.8	81.8	[0]	47							
Cycloheptene	−1.8	−1.8	[0]	39													
1,3-Cycloheptadiene	22.9	22.9	[0]	39													
1,3,5-Cycloheptatriene	44.5	44.5	[0]	40	1		75.4	75.4	[0]	47							
1-Methylcycloheptene	−10.5	−10.7	0.2	27[a,b]													
Methylenecycloheptane	−8.2	−6.7	−1.5	27[a–c]													
Cyclooctane	−29.7	−29.7	[0]	25	2^3		87.7	87.7	[0]	47							
cis-Cyclooctene	−6.2	−6.2	[0]	39													
trans-Cyclooctene	3.1	3.1	[0]	41													
1,3,5-Cyclooctatriene	43.7	43.7	[0]	42[a]													
Cyclooctatetraene	71.3	71.3	[0]	42[a]													
Cyclononane	−31.8	−31.8	[0]	25													
cis-Cyclononene	−7.2	−7.2	[0]	41[a]													
trans-Cyclononene	−4.3	−4.3	[0]	41[a]													
trans-Decalin	−43.6	−42.8	−0.8	43													
cis-Decalin	−40.4	−41.2	0.8	43													
Tetralin	2.6	6.6	−4.0	44[d]													
Hydrindene	14.3	14.8	−0.5	29													
trans-Hydrindane	−31.5	−31.4	−0.1	45													
Spiropentane	44.23	44.23	[0]	46	2^2		67.46	67.46	[0]	48	21.19	21.19	0	47.91	47.91	[0]	47
Bicyclo[1.1.0]butane	51.9	53.3	−1.4	*e*	2		62.49	52.49	[0]	69							
1,3-Dimethylcyclo[1.1.0]butane	39.3	37.9	−1.4	26													
Bicyclo[2.1.0]pentane	37.6	37.6	[0]	28[a]													
Bicyclo[3.1.0]hexane	9.07	9.07	[0]	50													
Bicyclo[4.1.0]hexane	0.32	0.32	[0]	49													
Bicyclo[5.1.0]octane	−3.87	−3.87	[0]	50													
Bicyclo[6.1.0]nonane	−7.42	−7.42	[0]	50													
1,4-Dihydronaphthalene	33.3	33.3	[0]	51													
1,2-Dihydronaphthalene	30.3	30.6	0.3	51													

[a] 1.0 kcal/mole added to heats derived from measurements in solution. [b] Depends upon the group value of the corresponding cycloalkane. [c] Using the ring correction of the corresponding cycloalkane. [d] Work done in 1910. [e] Added in proof: K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, **90,** 3395 (1968). [f] Added in proof: R. B. Tuiner, *et al.*, *ibid.*, **90,** 4315 (1968).

Table VIII

Alcohols and Phenols

Compound^{a}	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	*Estd*	Δ	*Ref*	n, σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Methanol,* CH_3OH	−48.0	−48.0	[0.0]	54	3	57.3	57.3	[0.0]	55	10.5	10.5	[0.0]	19.0	19.0	[0.0]	55
Ethanol, C_2H_5OH	−56.2	−56.5	+0.3	56	3	67.6	67.6	−0.1	56	15.7	15.5	0.2	30.3	30.1	0.2	56
1-Propanol, C_3H_7OH	−61.3	−61.5	+0.2	57	3	76.9	77.0	−0.1	57	20.9	21.0	−0.1	41.0	41.2	−0.2	58
1-Butanol, C_4H_9OH	−65.7	−66.4	+0.7	57	3	86.5	86.4	0.1	57							
1-Pentanol, $C_5H_{11}OH$	−71.9	−71.4	−0.5	59	3	96.1	95.8	0.3	*k*							
1-Hexanol, $C_6H_{13}OH$	−76.8	−76.3	−0.5	59												
1-Heptanol, $C_7H_{15}OH$	−81.7	−81.3	−0.4	59												
1-Octanol, $C_8H_{17}OH$	−86.6	−86.2	−0.4	59												
1-Nonanol, $C_9H_{19}OH$	−91.5	−91.2	−0.3	59												
1-Decanol, $C_{10}H_{21}OH$	−96.4	−96.1	−0.3	59												
2-Methyl-1-propanol, $(CH_3)_2CHCH_2OH$	−67.9	−67.7^{b}	−0.2	60	3^2	83.6	83.8	−0.2	*k*							
Allyl alcohol,* CH_2CHCH_2OH	−29.6	−29.6	[0.0]	61												
Benzyl alcohol,* $C_6H_5CH_2OH$	−22.5	−22.5	[0.0]	62												
Ethylene glycol, $C_2H_4(OH)_2$	−92.4	−92.8^{c}	+0.4	63	2	77.3	77.4	−0.1	64							
2-Propanol $(CH_3)_2CHOH$	−65.2	−65.1	−0.1	65	3^2	74.1	74.5	−0.4	65	21.3	21.5	−0.2	42.1	41.8	0.3	65
2-Butanol $(CH_3CH_2)(CH_3)CHOH$	−69.8	−70.1	+0.3	66	$2, 3^2$	85.8	85.3^{f}	0.5	66	27.2	27.0	+0.2	52.7	52.9	−0.2	66
Cyclopentanol, $(CH_2)_4CHOH$	−58.0^{d}	−58.4	+0.4	67												
Cyclohexanol, $(CH_2)_5CHOH$	−68.5^{e}	−69.7	+1.2	67												
2-Methyl-2-propanol,* $(CH_3)_3COH$	−74.7	−74.7	[0.0]	68	3^4	78.0	78.0	[0.0]	68	27.2	27.2	[0.0]	53.3	53.3	[0.0]	68
Methanediol,* $CH_2(OH)_2$	−93.5^{g}	−93.5	[0.0]	54												
Ethane-1,1-diol,* $CH_3CH(OH)_2$	−103.1^{h}	−103.1	[0.0]	69												
Phenol, C_6H_5OH	−23.1	−23.2	0.1	70	2	75.1	75.2	−0.1	71	24.8	24.2	0.6	50.7	50.6	0.1	71
o-Cresol, $CH_3C_6H_4OH$	−30.7	−30.5^{i}	−0.2	70	3	85.5	83.9^{i}	1.6	72	31.2	31.2^{i}	0.0	61.6^{i}	62.0	−0.4	72
m-Cresol, $CH_3C_6H_4OH$	−31.6	−31.1	−0.5	70	3	85.3	85.5	−0.2	72	29.8	30.1	−0.3	61.3	61.1	0.2	72
p-Cresol, $CH_3C_6H_4OH$	−30.0	−31.1	1.1	70	2 × 3	83.1	84.1	−1.0	72	29.8	30.1	−0.3	61.1	61.1	0.0	72
2,3-Xylenol, $(CH_3)_2C_6H_3OH$	−37.6	−37.8^{j}	0.2	70												
2,4-Xylenol, $(CH_3)_2C_6H_3OH$	−39.0	−38.5^{i}	−0.5	70												
2,5-Xylenol, $(CH_3)_2C_6H_3OH$	−38.7	−38.4^{i}	−0.3	70												
2,6-Xylenol, $(CH_3)_2C_6H_3OH$	−38.7	−37.8^{j}	−0.9	70												
3,4-Xylenol, $(CH_3)_2C_6H_3OH$	−37.4	−38.4^{i}	1.0	70												
3,5-Xylenol, $(CH_3)_2C_6H_3OH$	−38.6	−39.0	0.4	70												

[a] Compounds marked with an asterisk were the sole source for determining a particular group value. The data for these compounds necessarily fit the group predictions. [b] One *gauche* correction 0.8. [c] Using a calculated value of $\Delta H_{vap} = +16.3$. [d] Using a calculated value of $\Delta H_{vap} = 13.8$. [e] Using a calculated value of $\Delta H_{vap} = 15$. [f] Including $R \ln 2$ for optical activity. [g] Using $\Delta H_{aquation} = 1.6$ and $\Delta H_{vap} = 16$. [h] Using $\Delta H_{aquation} = 1.6$ and $\Delta H_{vap} = 16.3$ (*cf.* ethylene glycol). [i] One *ortho* correction. [j] Two *ortho* corrections. [k] Added in proof: J. F. Connsell, *et al.*, *J. Chem. Soc.*, *A*, 1819 (1968).

Table IX

Ethers^{a}

Compound	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	*Estd*	Δ	*Ref*	σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Dimethyl ether, CH_3OCH_3	−44.0	−43.2	−0.8	73	2×3^2	63.7	63.7*	[0.0]	74	15.8	15.8*	[0.0]	30.4*	30.4*	[0.0]	74
Methyl ethyl ether, $CH_3OC_2H_5$	−51.7	−51.7	−0.0	73												
Diethyl ether, $C_2H_5OC_2H_5$	−60.3	−60.2	−0.1	75												

Methyl *n*-propyl ether, $CH_3OC_3H_7$	−56.8	−56.7	−0.1	73
Methyl propyl ether, $CH_3OCH(CH_3)_2$	−60.2	−60.0[b]	−0.2	73
Di-*n*-propyl ether, $C_3H_7OC_3H_7$	−70.0	−70.1	+0.1	76
Diisopropyl ether, $(CH_3)_2CHOCH(CH_3)_2$	−76.1	−76.8[c]	+0.7	76
Di-*n*-butyl ether, $C_4H_9OC_4H_9$	−79.8	−80.0	+0.2	76
Di-*sec*-butyl ether, $(CH_3CH_2CH(CH_3))_2O$	−86.2	−85.7[d]	−0.5	76
Methyl *t*-butyl ether, $CH_3OC(CH_3)_3$	−70.0	−69.3	−0.7	77
Isopropyl *t*-butyl ether, $(CH_3)_2CHOC(CH_2)_3$	−85.6	−86.2[e]	+0.6	77
Di-*t*-butyl ether,* $(CH_3)_3COC(CH_3)_3$	−87.2	−87.2[f]	[0.0]	77
Methyl phenyl ether, $CH_3OC_6H_5$	−18.0[g]	−18.0	0.0	78
Ethyl phenyl ether, $C_2H_5OC_6H_5$	−25.4[h]	−25.5	+0.1	78
Diphenyl ether,* $C_6H_5OC_6H_5$	−10.1[i]	−10.1	[0.0]	79
Divinyl ether,* $CH_2CHOCHCH_2$	−3.0	−3.0	[0.0]	75
Ethyl vinyl ether, $C_2H_5OCHCH_2$	−33.5	−33.3	−0.2	75
2-Ethoxyprop-1-ene, $C_2H_5OC(CH_3)CH_2$	−43.4[j]	−43.4	0.0	61
2-Methoxy-*n*-but-2-ene, $CH_3OC(CH_3)CHCH_3$	−39.9[k]	−40.0	0.1	61
2,2-Dimethoxypropane, $(CH_3)_2C(OCH_3)_2$	−102.9	−103.3[l]	+0.4	80
2,2-Diethoxypropane, $(CH_3)_2C(OC_2H)_{52}$	−120.6	−102.3[l]	−0.3	80

[a] An asterisk denotes unique group. [b] One oxygen *gauche* correction of 0.3. [c] Two oxygen *gauche* corrections of 0.3. [d] Two oxygen plus two-alkyl *gauche* corrections. [e] Three oxygen *gauche* corrections. [f] Four oxygen *gauche* corrections plus strain. [g] Using calculated $\Delta H_{vap} = 11.6$. [h] Using calculated $\Delta H_{vap} = 12.3$. [i] From a heat of combustion of the solid plus heat of fusion of 4 and heat of vaporization of 15.2 (ref 79). [j] From a calculated heat of formation of −68.5 for ethyl isopropyl ether. [k] From a calculated heat of formation of −64.7 for methyl *sec*-butyl ether and includes one *cis* correction. [l] Includes four oxygen *gauche*.

Table X

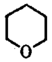
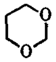
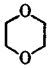
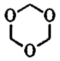
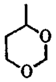
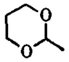
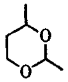
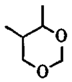
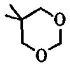
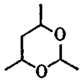
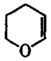
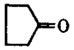
Peroxides and Hydroperoxides

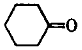
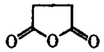
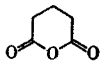
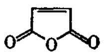
Compound	ΔH_f°					S°				$C_p{}^\circ{}_{300}$			$C_p{}^\circ{}_{800}$			
	Obsd	*Estd*	Δ	*Ref*	*n*, *σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Dimethyl peroxide, CH_3OOCH_3	−30.0	−29.2	−0.8	81												
Diethyl peroxide, $C_2H_5OOC_2H_5$	−46.1	−46.2	+0.1	81												
Di-*t*-butyl peroxide, $(CH_3)_3COOC(CH_3)_3$	−81.5	−81.6[a]	+0.1	81												
Hydrogen peroxide,[c] HOOH	−32.5	−32.5	[0.0]	82	2, 2	55.7	55.7	[0.0]	82	10.3	10.2	0.1	14.3	14.4	−0.1	82
t-Butyl hydroperoxide, $(CH_3)_3COOH$	−52.1	−57.1[b]	+5.0	83												
Hexyl-1 hydroperoxide	−58.6	−58.4	−0.2	84, 85												
Hexyl-2 hydroperoxide	−61.1	−62.9	+1.8	84, 85												
Hexyl-3 hydroperoxide	−59.9	−62.9	+3.0	84, 85												
Heptyl-1 hydroperoxide	−66.0	−63.4	−2.6	84, 85												
Heptyl-2 hydroperoxide	−66.8	−67.9	+1.1	84, 85												
Heptyl-3 hydroperoxide	−66.9	−67.9	+1.0	84, 85												
Heptyl-4 hydroperoxide	−63.8	−67.9	+4.1	84, 85												
Cyclohexyl hydroperoxide	−52.3	−52.8	+0.5	84, 85												
Methyl cyclohexyl hydroperoxide	−63.0	−59.8	−3.2	84, 85												
Acetyl peroxide, $(CH_3COO)_2$	−119.0	−129.0	+10.0	87												
Propionyl peroxide, $(C_2H_5COO)_2$	−138.0	−139.0	+1.0	87												
Butyryl peroxide, $(C_3H_7COO)_2$	−150.0	−149.0	−1.0	87												

[a] Including four oxygen *gauche* corrections. [b] Including two oxygen *gauche* corrections. [c] Gives unique group.

Table XI

Cyclics

Compound^a		$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
		Obsd	Estd	Δ	Ref	n, σ	Obsd	Estd	Δ	Ref	Obsd	Estd	Δ	Obsd	Estd	Δ	Ref
Ethylene oxide		−12.6	−13.1	0.5	88	2	58.0	58.4	−0.4	89	11.5	11.4	0.1	24.6	24.3	0.3	90
Propylene oxide		−22.2	−21.7	−0.5	91	2,3	68.5	68.6	−0.1	91	17.4	17.4	0.0	35.7	36.0	−0.3	91
Trimethylene oxide*		−19.3	−19.3	[0.0]	88	2	63.4	63.4	[0.0]	92	14.3	14.3	[0.0]	35.1	35.1	[0.0]	92
Tetrahydrofuran*		−44.0	−44.0	[0.0]	88												
Tetrahydropyran*		−53.5	−53.5	[0.0]	88												
1,3-Dioxane		−83.6	−83.6	0.0	94												
1,4-Dioxane*		−76.0	−76.0	[0.0]	93												
sym-Trioxane*		−120.8	−120.8	[0.0]	93												
4-Methyl-1,3,dioxane		−90.4	−92.2	+1.8	94												
2-Methyl-1,3,dioxane		−95.4	−93.2	−2.2	94												
cis-2,4-Dimethyl-1,3-dioxane		−102.3	−101.8	−0.5	94												
trans-4,5-Dimethyl-1,3-dioxane		−98.1	−98.4^b	+0.3	94												
5,5-Dimethyl-1,3-dioxane		−100.6	−97.7^c	−2.9	94												
2-*cis*,4-*trans*,6-trimethyl-1,3-dioxane		−106.1	−109.3^d	+3.2	94												
Furan*		−8.3	−8.3	[0.0]	95												
Dihydropyran		−29.9	−29.9	[0.0]	79												
Cyclopentanone*		−45.5	−45.5	[0.0]	67, 96												

Cyclohexanone*		−53.1	−53.1	[0.0]	96, 67
Succinic anhydride*		−122.6	−122.6	[0.0]	97
Glutaric anhydride*		−131.3	−131.3	[0.0]	97
Maleic anhydride*		−97.9	−97.9	[0.0]	98

[a] An asterisk denotes unique group. [b] Including one hydrocarbon *gauche* correction. [c] Including two oxygen *gauche* corrections. [d] Including one oxygen and one hydrocarbon *gauche* corrections.

Table XII

Aldehydes and Ketones

	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
Compound[a]	*Obsd*	*Estd*	Δ	*Ref*	σ	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
Acetaldehyde, CH_3CHO	−39.7	−39.7	[0.0]	99	3	63.2	63.2	[0.0]	99	13.2	13.2	[0.0]	24.2	24.2	[0.0]	99, 100
Propionaldehyde, C_2H_5CHO	−45.6	−44.7	−0.9	57, 101	3	73.4	72.7	0.7	101	18.8	19.4	−0.6	35.2	35.3	−0.1	101
Butyraldehyde, C_3H_7CHO	−48.9	−49.7	+0.8	57	3	82.6	82.1	0.5	57							
Heptaldehyde, $C_6H_{13}CHO$	−62.8	−64.7	+1.9	57												
Acetone,* CH_3COCH_3	−51.7	−51.7	[0.0]	102	2 × 3^2	70.5	70.5	[0.0]	102	18.0	18.0	[0.0]	34.9	34.9	[0.0]	102
Methyl ethyl ketone, $CH_3CH_2COCH_3$	−57.0	−56.7	−0.3	103	3^2	80.8	81.5	−0.7	103	24.7	24.2	0.5	46.1	46.0	0.1	103
Diethyl ketone	−61.65	−61.56	−0.9	105	2 × 3^2	88.6	89.3	−0.7	*e*							
Methyl *n*-propyl ketone	−61.92	−61.56	−0.36	105	3^2	90.5	90.8	−0.3	*e*							
Ethyl *n*-propyl ketone	−66.51	−66.51	0	105												
Methyl *n*-butyl ketone	−66.96	−66.51	−0.45	105												
Di-*n*-butyl ketone	−82.57	−81.36	−1.21	105												
Methyl isopropyl ketone	−62.76	−63.07	+0.31	105	3^3	88.5	88.1	0.4	*e*							
Ethyl isopropyl ketone	−68.38	−68.02	−0.36	105												
Diisopropyl ketone	−74.40	−74.44	+0.04	105												
Ethyl *t*-butyl ketone	−75.00	−74.69	+0.31	105												
Isopropyl *t*-butyl ketone	−80.84	−81.15	+0.31	105												
t-Butyl neopentyl ketone	−94.15	−93.32	−0.83	105												
Di-*t*-butyl ketone	−82.65	−87.83	+5.18	105												
Crotonaldehyde,* $CH_3CHCHCHO$	−25.5	−25.5	[0.0]	61												
Furfuraldehyde*	−35.4	−34.4[b]	0.0	104												
Benzaldehyde,* C_6H_5CHO	−6.0	−6.0	[0.0]	52												
Acetophenone,* $C_6H_5COCH_3$	−22.0	−22.0	[0.0]	85												
Benzophenone,* $C_6H_5COC_6H_5$	12.3	12.3	[0.0]	85												
Acetylacetone,* $CH_3COCH_2COCH_3$	−90.4	−90.4[c]	[0.0]	106												
Diacetyl, $CH_3COCOCH_3$	−78.6	−78.6[d]	[0.0]	62												

[a] An asterisk denotes unique group. [b] Heat of vaporization estimated to be 12 kcal/mole. [c] Heat of vaporization estimated to be 11 kcal/mole. [d] Heat of vaporization estimated to be 9 kcal/mole.
[e] Added in proof: R. J. L. Anden, *et al.*, *J. Chem. Soc.*, *A*, 1894 (1968).

Table XIII

Acids, Esters, and Anhydrides

Compound[a]	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	Estd	Δ	Ref	σ	Obsd	Estd	Δ	Ref	Obsd	Estd	Δ	Obsd	Estd	Δ	Ref
Formic acid, $HCOOH$	−90.5	−89.9	−0.6	98	1	59.4	59.4	0.0	98	10.8	10.8	0.0	18.3	18.4	−0.1	98
Acetic acid, CH_3COOH	−103.8	−103.8	0.0	107, 108	3	67.5	68.3	−0.8	107	16.0	16.0	0.0	29.1	29.1	0.0	107
Methyl formate, $HCOOCH_3$	−81.0	−81.0	0.0	52	3	84.6	72.3	12.3	52							
Ethyl acetate, $CH_3COOC_2H_5$	−103.4	−103.4	0.0	52	3^2	90.1	89.9	0.2	52							
Methyl benzoate, $C_6H_5COOCH_3$	−71.7	−71.2	−0.5	85												
Ethyl benzoate, $C_6H_5COOC_2H_5$	−79.1	−79.7	+0.6	85												
Vinyl acetate,* $CH_3COOCHCH_2$	−72.4	−72.4	[0.0]	52, 61												
Methyl methacrylate,* $CH_2C(CH_3)COOCH_3$	−79.3[b]	−79.3	[0.0]	61												
Methyl *trans*-cinnamate, $C_6H_5CHCHCOOCH_3$	−49.3[c]	−48.2	−1.1	109												
Diethyl fumarate, $(CHCOOC_2H_5)_2$	−168.9[d]	−170.1	+1.2	109												
Acetic anhydride,* $(CH_3CO)_2O$	−137.9	−137.9	[0.0]	97												

[a] An asterisk denotes unique group. [b] Using a calculated value of −107.9 for methyl isobutyrate. [c] Using a calculated value of −79.0 for methyl β-phenylpropionate. [d] Using a calculated value of −198.2 for diethyl succinate.

Table XIV

Aliphatic and Aromatic Amines[a]

										300°K			800°K			
	$\Delta H_f°$					$S°$				$C_p°$			$C_p°$			
Compound	Obsd	Estd	Δ	Ref	n, σ	Obsd	Estd	Δ	Ref	Obsd	Estd	Δ	Obsd	Estd	Δ	Ref
						Aliphatic Amines										
CH_3NH_2	−5.5	−5.3	−0.2	110	3	57.93*	57.93	[0.0]	111	11.91*	11.91	[0.0]	22.43*	22.43	[0.0]	111
$(CH_3)_2NH$	−4.5	−4.8	0.3	110	3^2	65.39*	65.39	[0.0]	112	16.58*	16.58	[0.0]	33.94*	33.94	[0.0]	112
$(CH_3)_3N$	−5.9	−5.8	−0.1	110	3^4	69.15*	69.15	0.0	112	22.05*	22.05	[0.0]	45.62*	45.62	[0.0]	112
$C_2H_5NH_2$	−11.0	−11.9	0.9	110		...	67.7			...	17.56		...	33.52		
$(C_2H_5)_2NH$	−17.2	−18.0	0.8	110		...	85.0			...	27.08		...	56.12		
$(C_2H_5)_3N$	−23.9	−23.2	−0.7	110		...	98.4			...	37.80		...	78.89		
n-$C_3H_7NH_2$	−16.77	−16.80	0.03	120												
i-$C_3H_7NH_2$	−20.02	−20.6	0.58	120												
n-$C_4H_9NH_2$	−21.8	−22.8	1.0	113[b]		...	86.6			...	28.16		...	55.66		
sec-$C_4H_9NH_2$	[−24.7]*	−24.7	[0.0]	113[b]		...	83.9			...	28.27		...	56.08		
t-$C_4H_9NH_2$	−28.6*	−28.6	[0.0]	113[b]		...	78.3			...	28.64		...	56.96		
n-C_4H_9NH-*i*-C_4H_9	−40.2	−39.1	−1.1	113[c]		...	120.0			...	48.81		...	100.59		
						Aromatic Amines										
$C_6H_5NH_2$	20.8*	20.8	[0.0]	115	2	76.44*	76.44	[0.0]	115	26.07*	26.07	[0.0]	53.79*	53.79*	[0.0]	115
$C_6H_5NHCH_3$	21.6	20.8	0.8	116												
$C_6H_5N(CH_3)_2$	22.8	22.0	0.8	116												
$C_6H_5NHC_2H_5$	13.4	14.2	−0.8	117												
$C_6H_5N(C_2H_5)_2$	9.6	10.4	−0.8	117												
$(C_6H_5)_2NH$	49.9*	49.9	[0.0]	118 119												

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions. [b] $\Delta H_v°$ revised (see text). [c] $\Delta H_v°$ revised (see text) to 11.4 kcal/mole.

Table XV

Imines

Compound	$\Delta H_f°$ Obsd	$\Delta H_f°$ Estd	Δ	Ref	$S°$ Obsd	$S°$ Estd	300°K $C_p°$ Obsd	300°K $C_p°$ Estd	800°K $C_p°$ Obsd	800°K $C_p°$ Estd
$CH_3CH{=}N\text{-}n\text{-}C_3H_7$	−1.2	−1.6	0.8	121[a]						
$C_2H_5CH{=}NC_2H_5$	−0.0	−1.7	1.7	121[a]						
$C_2H_5CH{=}N\text{-}n\text{-}C_3H_7$	−8.1	−6.6	−1.5	121[a]						
$C_2H_5CH{=}N\text{-}i\text{-}C_3H_7$	−9.6	−9.6	0.0	121[a]						
$i\text{-}C_3HCH_7{=}NC_2H_5$	−7.5	−8.6	1.1	121[a]						
$i\text{-}C_3H_7CH{=}N\text{-}n\text{-}C_4H_9$	−20.4	−18.5	−1.9	114[b]						

[a] $\Delta H_f°$ for *all* the others calculated from liquid-phase heats of hydrogenation quoted in ref 121 as follows. To obtain gas-phase heats of hydrogenation 0.5 kcal/mole is added to liquid-phase values to allow for differences in $\Delta H_v°$. From these gas-phase heats of hydrogenation and group estimates of $\Delta H_f°$ for corresponding amines, $\Delta H_f°$ values for the imines were obtained. [b] $\Delta H_v°$ revised (see text) to 11.4 kcal/mole.

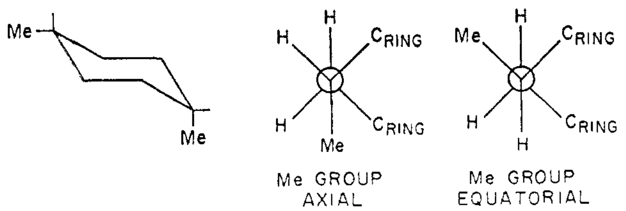


Figure 3.

Additional independent evidence for the size of the alkane *gauche* interaction is also obtained from the substituted cyclohexanes. For example, $\Delta H_f°$ for *cis*-1,4-dimethylcyclohexane is 1.9 kcal/mole greater than for the *trans* isomer. In Figure 3 we see that in the *trans* isomer the methyl groups can be all equatorial or all axial, whereas in the *cis* isomer there must always be one axial methyl group. From the Newman diagrams in Figure 3, it is seen that the axial methyl group has *gauche* interaction with each of the two next-nearest ring carbon atoms. This would lead to an expected decrease in stability by 2 × 0.8 = 1.6 kcal mole for the *cis* isomer, and this is very close to the observed 1.9 kcal/mole. For 1,3-dimethylcyclohexane, the opposite is true, *i.e.*, the *trans* isomer must have one axial methyl group, and we would predict it should be less stable than the *cis* isomer by 1.6 kcal/mole. The observed difference is 1.96 kcal/mole. In *trans*-1,2-dimethylcyclohexane, the two Me groups are equatorial, generating one *gauche* interaction. In the *cis* isomer, one Me group is equatorial and the other axial, generating three *gauche* interactions, since they are on adjacent carbon atoms. The observed difference in $\Delta H_f°$ is 1.87 kcal/mole, again equal to two *gauche* interactions within experimental error. *Gauche* interactions between ring carbon atoms are included in the ring correction.

This treatment of the cyclic compounds does not strictly adhere to our definition of the law of group additivity, since we cannot write disproportionation reactions that open the ring. However, this is generally a minor deviation.

Use of the open-chain hydrocarbon groups can cause some difficulties. For instance, the use of the values derived from conjugated dienes for the entropy of ring systems, like methylene–cyclobutene in conjunction with the entropy ring correction for cyclobutene itself, overcorrects for the stiffness of the ring since the diene has some stiffness already. In cases of this type, it is better to use the groups from unconjugated olefins.

Having established the ring corrections, we may use them to get group values from cyclic compounds. For instance, the heat of hydrogenation of 1,4-dihydronaphthalene to tetralin yields a value for the group $C\text{–}(C_B)(C_d)(H)_2$ if the ring correction for tetralin is taken as the sum of the strains in cyclohexene and that in 1,4-cyclohexadiene.

Such transferability of ring corrections must involve caution. For instance, the heat of formation of 1,2-dihydronaphthalene is predicted exactly, only if the ring correction is adjusted for the difference in conjugation energy of styrene and 1,2-dienes. Where ΔH_2 = heat of hydrogenation, the conjugation energies are defined as

$$\begin{aligned}\text{conjugation energy of styrene} &= \Delta H_{H_2}°(\text{styrene}) - \\ &\quad \Delta H_{H_2}°(\text{mono-1-olefin}) = 1.7\ \text{kcal/mole}\\ \Delta H_{H_2}°(\text{styrene}) &= [C_B\text{–}(C)] - [C_B\text{–}(C_d)] + [C\text{–}(C)(C_B)(H)_2] - \\ &\quad [C_d\text{–}(C_B)(H)] - [C_d\text{–}(H)_2] + [C\text{–}(H)_3(C)]\\ \Delta H_{H_2}(\text{mono-1-olefin}) &= [C\text{–}(C)_2(H)_2] - [C\text{–}(C_d)(C)(H)_2] + \\ &\quad [C\text{–}(C)_2(H)_2] - [C_d\text{–}(C)(H)] - [C_d\text{–}(H)_2] + [C\text{–}(H)_3(C)]\end{aligned}$$

$$\begin{aligned}\text{conjugation energy of 1,3-dienes} &= \Delta H_{H_2}°(\text{diene} - \\ &\quad \Delta H_{H_2}°(\text{mono-1-olefin}) = 4.07\ \text{kcal/mole}\\ \Delta H_{H_2}°(\text{1,3-diene}) &= [C_d\text{–}(C)(H)] + [C\text{–}(C_d)(C)(H)_2] - \\ &\quad [2C_d\text{–}(C_d)(H)] + [C\text{–}(C)(H)_3] - [C_d\text{–}(H)_2]\end{aligned}$$

Thus, the ring correction for 1,2-dihydronaphthalene becomes

$$\text{ring correction (cyclohexadiene-1,3)} - (4.0 - 1.7) = 2.5\ \text{kcal/mole}$$

In conclusion, we may summarize the usefulness of the law of group additivity, as applied to hydrocarbons, as follows. In the prediction of entropy and heat capacity, the additivity of group properties generally gives agreement with experiment within ±0.5 gibbs/mole. In the estimation of heats of formation, the agreement is generally in the range ±0.5 kcal/mole. For hydrocarbons, enough data of this type exist to make suspect any data which deviates from group additivity by more than 1 gibbs/mole or 1 kcal/mole. Exceptions to this rule will appear in the case of very heavily branched compounds.

This section prepared by S. W. Benson, H. E. O'Neal, and D. M. Golden.

IV. Oxygen-Containing Compounds

The three main sources of original data used were the Benson and Buss paper,[2] a valuable review by Green,[52] and the IUPAC Bulletins of Thermodynamics and Thermochemistry.[53]

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(52) J. H. Green, *Quart. Rev.* (London), **15**, 125 (1961).

(53) Bulletins of Thermodynamics and Thermochemistry, IUPAC, University of Michigan, Ann Arbor, Mich.

The group values are in Table XXXIV. In Tables VIII–XIII,[54–109] observed data are compared with those estimated from groups. There are more groups and less observed data for oxygen compounds than for hydrocarbons. Consequently, there are many more sole sources for groups. But in the cases where there is enough information to make a reasonable test, such as in the heats of formation of the alcohols and ethers, it is clear that the principle of group additivity is valid. Compared with the number of heats of formation, there are very few entropies and heat capacities. For example, it is surprising that dimethyl ether is the only aliphatic ether for which the entropy or heat capacity has been measured.

The data are insufficiently precise or extensive to fix a good value for the *gauche* interactions in branched compounds. The value selected (0.3 kcal/mole) fits the data quite well, but values smaller or larger by 0.2 kcal/mole would do about as well.

This section prepared by S. W. Benson and R. Shaw.

V. Nitrogen-Containing Compounds

As with the oxygen-containing compounds, there are much less data for the nitrogen compounds than for the hydrocarbons. Consequently, the accuracy of the nitrogen groups is more variable and not so high as for the hydrocarbons. In some cases interpolation methods and similar approximations have been necessary to obtain a group value. No values are available for nitrogen compounds containing carbonyl groups, halogen atoms, etc., so that any complex intramolecular interactions in such compounds cannot be included in any estimate by group additivity.

A. AMINES

1. Aliphatic

The data and group predictions are presented in Table XIV.[110–120] In order to obtain the estimates for entropy and specific heats for all except the three methylamines, group values were used which have been obtained from compounds (RNH_2) by interpolating between the corresponding alcohols (ROH) and alkanes (RCH_3). This procedure was checked for CH_3NH_2, taking the arithmetic mean of values for CH_3OH and CH_3CH_3 (symmetry corrected for the entropy). The errors involved were less than 0.5 eu.

Some of the gas-phase heats of formation were suspected to be slightly in error, due to errors in estimated or measured heats of vaporization. These we revised, using Trouton's rule (and in the case of these amines, a Trouton constant, $S_T = 22$ eu, which may still be a trifle low) and corrected to 25°, using $\Delta C_p(\text{vap}) \simeq 15$ eu.

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2. *Aromatic*

The data and group predictions are shown in Table XIV. It should be noted at this point that for single side chains attached to benzene rings the possibility of nonbonded steric interactions arises, even if the side chains are unbranched. For instance, in N-methylaniline, by analogy with ethylbenzene, the terminal methyl group, will be close ($\leq 90°$) to one or other of the *ortho* positions of the benzene ring. This interaction cannot be classed as *gauche* in the strictest sense, and for simplicity's sake we have included it in the relevant group. For example, $C_6H_5N(C_2H_5)_2$ has only two "*gauche*" corrections worth 1.6 kcal/mole in all.

B. IMINES

As can be seen from Table XV,[121] only ΔH_f° values are known for a few imines, but the internal consistency is fairly reasonable.

In Table XXXV, as stated, the N_I refers to the nitrogen in these compounds. In order to separate this group value from others in the molecule, the carbon atom end of the double bond was taken as a C_d atom (as in olefins), and it was assumed that the groups, $C-(N_I)(C)(H)_2$, $C-(N_I)(C)_2(H)$, were the same as $C-(N)(C)(H)_2$, $C-(N)(C)_2(H)$. This assumption holds well for olefins where it can be seen that $C-(C_d)(C)(H)_2$ is almost the same as $C-(C)_2(H)_2$.

C. CYANIDES (OR NITRILES)

The data are compared with the group predictions in Table XVI.[122–136] Recent ΔH_f° values for alkyl cyanides are particularly sparse. A check on the group predictions for ethyl cyanide would be particularly valuable, for instance. The deviations observed for *trans*-dicyanoethylene may be real and may indicate a conjugation of electrons sufficient to cause departure from group additivity.

D. NITRO COMPOUNDS

The data are compared with group predictions in Table XVII. Since the only entropy data for nitro compounds were those of CH_3NO_2, it was necessary to use bond additivity to generate the entropy estimates listed here. It was from these estimates (symmetry corrected) that the group values listed in Table XXXV were calculated.

Table XVI

Cyanides[a]

Compound	ΔH_f°		Δ	Ref	n, σ	S°		Δ	Ref	300°K			800°K			
										C_p°			C_p°			
	Obsd	Estd				Obsd	Estd			Obsd	Estd	Δ	Obsd	Estd	Δ	Ref
C_2H_5CN	...	12.4	...	...		68.75	68.4	0.35	123	17.30*	17.30	[0.0]	32.7*	32.7	[0.0]	122
n-C_3H_7CN	7.45*	7.45	[0.0]	124		...	77.8	...	...	...	22.8	...	...	43.8	...	...
i-C_3H_7CN	5.62*	5.62	[0.0]	124		...	76.2	...	...	...	23.4	...	...	43.4	...	...
C_6H_5CN	52.3*	52.3	[0.0]	124		76.89*	76.89	[0.0]	125	26.2*	26.2	[0.0]	52.1*	52.1	[0.0]	125
c-C_3H_5CN	...	43.5	...	...		70.7*	70.7	[0.0]	126[b]	18.95*	18.95	[0.0]	37.68*	37.68	[0.0]	126
$NCCH_2CH_2CN$	...	45.0	...	...		79.10	79.0	0.1	127	...	22.2	...	...	39.4	...	...
$NCCH_2CH_2CH_2CN$	...	40.0	...	...		88.1	88.51	−0.41	128	...	27.7	...	...	50.5	...	...
$(CH_3)_3CCN$	...	...	...	...		79.63*	79.63	[0.0]	134	...	...	...	...	...	...	...
$CH_2{=}CHCN$	43.7	43.6	0.1	130		65.56	64.20	1.36	129	15.30	14.90	0.4	26.43	26.4	0.03	129
trans-$CH_3CH{=}CHCN$	35.8	35.9	−0.1	131		71.43	72.8	−1.37	131	19.71	20.10	−0.39	36.97	37.0	−0.03	131
trans-$NCCH{=}CHCN$	81.3	74.8	6.5	136		...	...	...	...	...	...	...	...	...	...	...
$C_2H(CN)_3$	123.9	122.5	1.4	132		...	...	...	...	...	...	...	...	...	...	...
$C_2(CN)_4$	168.5	171.3	−2.8	132		...	...	...	...	...	...	...	...	...	...	...
$C_2(CN)_2$	127.5*	127.5	[0.0]	133		69.44*	69.44	[0.0]	133	20.58*	20.60	[0.0]	27.26*	27.26	[0.0]	133
$(CH_3)_2C(CN)_2$	...	...	...	...		83.42*	83.42	[0.0]	135	...	...	...	...	...	...	...

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions. [b] Note the quoted value for S° in ref 126 is in error.

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Table XVII

Nitro Compounds[a]

Compound	$\Delta H_f°$ Obsd	$\Delta H_f°$ Estd	Δ	Ref	n, σ	S° Obsd	S° Estd	300°K $C_p°$ Obsd	300°K $C_p°$ Estd	800°K $C_p°$ Obsd	800°K $C_p°$ Estd
$C_2H_5NO_2$	−23.8	−24.4	0.6	139[b]	3 × 2		75.2				
n-$C_3H_7NO_2$	−29.7	−29.3	−0.4	139	3 × 2		84.6				
i-$C_3H_7NO_2$	−33.9	−34.4	0.5	139	3^2 × 2		82.0				
n-$C_4H_9NO_2$	−34.4	−34.3	−0.1	139	3 × 2		94.0				
sec-$C_4H_9NO_2$	−39.1	−38.5	−0.6	139	3^2 × 2		91.4				
$C_2H_5CH(NO_2)_2$	−25.9*	−25.9	[0.0]	139							

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions. [b] $\Delta H_v°$ revised to 9.7 kcal/mole.

E. NITRITES AND NITRATES

The data are compared with group predictions in Table XVIII. Heats of vaporization were generally consistent with a Trouton constant of 22.5 eu, for both classes of compounds, with the exception of $\Delta H_v°$ (n-C_3H_7ONO). Consequently, the latter was revised in accordance with S_T = 22.5 eu.

F. HYDRAZINES, AZO COMPOUNDS, AND TETRAZINES

The data are compared with group predictions in Table XIX.[145–150] Information on azo compounds is particularly lacking. It is interesting to note here a much quoted value for $\Delta H_f°(CH_3N{=}NCH_3)$ of 43.2 kcal/mole.[137] This value was never measured, but merely estimated from $\Delta H_f°(i\text{-}C_3H_7N{=}NiC_3H_7)$[138] by a cruder additivity rule, which is, in principle, less reliable than that used in this paper. The data of Table XXXV would predict $\Delta H_f°(CH_3N{=}NCH_3)$ = 44.7 kcal/mole. It should be pointed out, however, that in deriving the group values for azo compounds, it was assumed that the increments in replacing H by Me in CH_3NNCH_3 were the same as the corresponding increments in the isoelectronic olefins $CH_3CHCHCH_3$.

G. AMIDES AND IMIDES

The data are compared with group predictions in Table XX.[151–154] Unfortunately, there are no checks whatsoever on the group values for heats of formation among the amides, and therefore this table probably contains the least reliable information of any class of nitrogen-containing compounds listed thus far. However, the method of measuring heats of hydrolysis for many of these amides ought to give values for $\Delta H_f°$ at least as reliable as combustion measurements, and it is felt that these data are probably good to better than ±2 kcal/mole.

H. NITROGEN-CONTAINING RING COMPOUNDS

The data for saturated nitrogen-containing ring compounds are included as corrections to group predictions and listed in Table XXXV. Comparison of these ring corrections with those of sections III and IV shows once again that, both for heats and entropies, they tend to depend primarily on ring size and not significantly on whether a $>CH_2$ has been replaced by an $>O$ or an $>NH$ group. Such a rule has been used to estimate several of the ring corrections, where data are lacking. Application of this rule must obviously be made with caution, since the ring correction for $\Delta H_f°$ for succinimide appears to be slightly high for a five-membered ring. In this particular case, however, we feel the data and imide group values are not sufficiently reliable to predict this ring correction to better than ±2 kcal/mole and thus invalidate the rule.

The data for unsaturated, nitrogen-containing heterocyclic ring compounds (most $\Delta H_f°$ values) are listed in Table XXI.[155–162] These data do not readily extend themselves to the method of ring corrections by group predictions, since all of these compounds show resonance. The problem of estimation of the resonance energies involved depends on establishment of a proper standard of comparison. This is rather an involved and complex problem, and we feel that it would not be appropriate to discuss it here, particularly since it would not contribute to the task of empirical prediction.

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Table XVIII

Nitrites and Nitrates[a]

	ΔH$_f$°					S°				300°K C$_p$°			800°K C$_p$°			
Compound	*Obsd*	*Estd*	Δ	*Ref*	*n, σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
CH_3ONO	−15.6	−16.0	0.4	141	3	70.14*	70.14	[0.0]	140	15.36*	15.36	[0.0]	26.27*	26.27	[0.0]	140
C_2H_5ONO	−24.2	−24.5	0.3	85	3	...	80.6	...	...	...	20.35	...	...	37.38	...	
n-C_3H_7ONO	−30.1	−29.4	−0.7	85[f]	3	...	90.10	...	...	...	25.85	...	...	48.45	...	
CH_3ONO_2	−28.6	−28.7	0.1	142, 141	3 × 2	75.97	75.30	0.67	143	...	...	...	...	...	...	
$C_2H_5ONO_2$	−36.8	−37.2	0.4	85	3 × 2	85.14	85.80	−0.66	144	...	...	...	...	...	...	
n-$C_3H_7ONO_2$	−41.8	−42.1	0.3	85	3 × 2	...	95.20	...	...	...	...	...	...	...	...	
i-$C_3H_7ONO_2$	−45.7	−45.0	−0.7	85	3^2 × 2	...	92.20	...	...	...	...	...	...	...	...	

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions. [b] ΔH$_v$° revised to 7.9 kcal/mole.

Table XIX

Hydrazines, Azo Compounds, and Tetrazines

	ΔH$_f$°					S°				300°K C$_p$°			800°K C$_p$°			
Compound	*Obsd*	*Estd*	Δ	*Ref*	*n, σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
N_2H_4	22.8	22.8	0.0	133	2, 2	57.03	56.9	0.13	133	12.19*	12.19	[0.0]	21.08*	21.08	[0.0]	133
CH_3NHNH_2	22.3	22.2	0.1	146	2, 1	66.72	67.0	−0.28	145	17.1*	17.1	[0.0]	31.3*	31.3	[0.0]	145
$CH_3NHNHCH_3$	21.6	21.6	0.0	146	2, 2	74.39	74.3	0.09	147	...	22.0	...	...	41.6	...	
$(CH_3)_2NNH_2$	20.4	20.4	0.0	148, 149	2, 1	72.82	71.80	1.02	148	...	...	...	...	...	...	
$(CH_3)_2NNHCH_3$	...	20.7	....	...	2, 1	79.45	80.50	−1.05	150	...	...	...	...	...	...	
$C_6H_5NHNH_2$	50.1	50.3	−0.2	118, 119				...	...			...			...	
$C_6H_5NHNHC_6H_5$	77.9	77.8	0.1	118, 119				...	...			...			...	
$NH{=}NH$	50.2*	50.2	[0.0]	133		52.22*	52.22	[0.0]	133	8.75*	8.75	[0.0]	13.55*	13.55	[0.0]	133
i-$C_3H_3N{=}N$-i-C_3H_7	19.4*	19.5	[0.0]	138		...	...	...	...	...	...	...	...	...	...	
$(CH_3)_2NN{=}NN(CH_3)_2$	65.7*	65.7	[0.0]	149		...	...	...	...	...	...	...	...	...	...	

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions.

Table XX

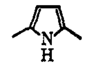
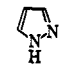
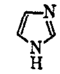
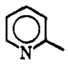
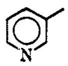
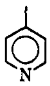
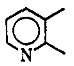
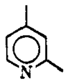
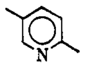
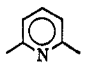
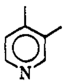
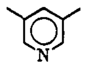
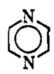
Amides and Imides[a]

	ΔH$_f$°					S°				300°K C$_p$°			800°K C$_p$°			
Compound	*Obsd*	*Estd*	Δ	*Rej*	*n, σ*	*Obsd*	*Estd*	Δ	*Rej*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
$HCONH_2$	−44.5*	−44.5	[0.0]	152	...	59.62*	59.62	[0.0]	151	11.10*	11.1	[0.0]	21.12*	21.10	[0.0]	151
CH_3CONH_2	−57.8*	−57.8	[0.0]	154	3	69.10*	69.1	[0.0]	153	15.63	15.63	[0.0]	32.60*	32.6	[0.0]	153
CH_3CONH-n-C_4H_9	−73.1*	−73.1	[0.0]	154[b]	3^2	...	105.2			...	...		...	...		
$CH_3CONHC_6H_5$	−24.9*	−24.9	[0.0]	154[b]	...	...	...			...	...		...	...		
$(CH_3CO)_2NH$	−102.7*	−102.7	[0.0]	154[b]	...	...	...			...	...		...	...		
$(CH_3CO)_2N$-n-C_4H_9	−114.2*	−114.2	[0.0]	154[b]	...	...	...			...	...		...	...		
$(CH_3CO)_2NC_6H_5$	−65.5*	−65.5	[0.0]	154[b]	...	...	...			...	...		...	...		

[a] Each piece of data marked with an asterisk was the sole source for determining a particular group value, and therefore these data necessarily fit the group predictions. [b] Calculated from the data of ref 154; known values for ΔH$_f$°(CH_3COOH) and ΔH$_f$°(H_2O) given in part IV and known or group estimates for ΔH$_f$° of various amines.

Table XXI

Heterocyclic N-Atom-Containing Ring Compounds in the Ideal Gas State (1 Atm)

Compound *Name*	*Formula*	ΔH_f° *Obsd*	ΔH_f° *Estd*[a]	Δ	*Ref*	*n*, σ	S° (*obsd*)	*Ref*	*300°K* $C_p{}^\circ{}_{300}$ (*obsd*)	*800°K* $C_p{}^\circ{}_{800}$ (*estd*)	*Ref*
Pyrrole		25.88		...	155	2	64.66		17.16	38.38	
2,5-Dimethylpyrrole		9.1		...	119	...					
Pyrazole		43.3		...	114	...					
Imidazole		30.6		...	114	...					
Pyridine		33.5	33.2	0.3	156	2	67.7	159	18.80	42.49	157
Picolines, α		23.6	23.8	−0.2	158	3	77.8	160	24.05	53.21	158
β		25.3	25.3	0.0	159	3	77.8	161	23.94	53.12	159
γ		24.4	23.8	0.6	160	...					
Dimethylpyridines (lutidines) 2,3		16.3	16.5	−0.2	161	...					
2,4		15.3	14.4	0.9	161	...					
2,5		15.9	15.9	0.0	161	...					
2,6		14.0	14.4	−0.4	161	...					
3,4		16.7	16.5	0.2	161	...					
3,5		17.4	17.4	0.0	161	...					
Pyridazine		66.5		...	162	...					
Pyrimidine		47.0		...	162	...					
Pyrazine		46.9		...	162	...					

[a] See text for explanation of method of estimation.

There appear to be small, systematic differences in positional isomers in the pyridine-substituted compounds, favoring *ortho* and *para* substitution. The simplest way to bring these compounds into the system of ring corrections is to use the N_I-(C_B) group to define the pyridine ring, and then make a −1.5 kcal correction for the extra stability due to *ortho* and *para* substitution, and otherwise the same *ortho* corrections as in benzene. The agreement between estimates arrived at thus and observed ΔH_f° values is seen from Table XXI to be good. A comparison of these effects of methyl substitution with those for benzene itself $[\Delta H_f^\circ(C_6H_5CH_3) - \Delta H_f^\circ(C_6H_6) = 7.8$ kcal/mole] shows that methyl substitution on pyridine always produces a slightly greater stabilization than on benzene.

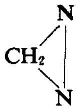
As far as the various isomeric heterocycles containing two ring nitrogen atoms are concerned, it is evident that isomers in which the nitrogen atoms are bonded to one another are significantly less stable than those in which they are not. This could have been qualitatively anticipated on the general grounds of electronegativity.

I. SOME UNIQUE GROUP COMPOUNDS

The above tables represent the extent of the comparison possible between existing data and group predictions. The group additivity method offers no rationale of the properties of particular low molecular weight compounds which are themselves unique groups. In addition, methods are available

Table XXII

Unique Groups

Compound	ΔH_f°	*Ref*	S°	*Ref*	C_p° *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*	*Ref*
NH_3	−10.98	133	46.09	133	8.53	9.24	10.04	10.81	12.23	13.47	15.85	133
HCN	32.3	133	48.27	133	8.61	9.42	10.04	10.56	11.45	12.18	13.48	133
CH_3CN	(19.1)[a]		58.2	165	12.55	14.66	16.65	18.42	21.32	23.55		165
$(CN)_2$	73.87	133	57.80	133	13.59	14.77	15.62	16.31	17.42	18.24	19.43	133
$CH_2(CN)_2$	63.5	136	69.16	166	17.38	20.22	22.61	24.60	27.72	30.00		166
HNC			48.78	167	9.33	9.97	10.44	10.83	11.49	12.06	13.10	167
CH_3NC	35.9	168	59.06	177	12.83	14.80	16.72	18.45	21.34	23.56		177
HN_3	71.6	169	57.14	169	10.46	11.74	12.81	13.71	15.10	16.12	17.68	169
CH_3N_3	67	170, 163										
CH_2N_2	71	172	58.11	171	12.58	14.23	15.62	16.87	18.73	20.19	22.52	171
	79	174	56.93	173	10.23	12.39	14.34	15.94	18.35	20.04		173
HCNO	−27.9	133	56.98	133	10.57	12.09	13.11	13.93	15.19	16.13	17.62	133
HNO	23.8	133	52.78	133	8.29	8.79	9.34	9.87	10.77	11.45	12.51	133
CH_3NO	(16)[a]											
HONO	−18.6	133	59.63	133	10.95	12.36	13.48	14.37	15.66	16.55	17.90	133
$HONO_2$	−32.1	133	65.12	133	12.80	15.10	16.93	18.35	20.33	21.61	23.42	133
CH_3NO_2	−17.9	175	65.81	175	13.76	16.80	19.56	21.92	25.56	28.17	32.05	175
N_2	0	133	45.77	133	6.96	6.99	7.07	7.20	7.51	7.82	8.33	133
NO	21.58	133	50.39	133	7.13	7.16	7.29	7.47	7.83	8.12	8.55	133
NO_2	7.91	133	57.40	133	8.85	9.60	10.33	10.96	11.88	12.47	13.20	133
NO_3 sym	16.6	133	60.42	133	11.26	13.37	14.96	16.11	17.51	18.28	19.12	133
NO_3 unsym	14	176	68	176								
N_2O	19.61	133	52.60	133	9.25	10.20	10.95	11.57	12.49	13.11	13.96	133
N_2O_3	19.8	133	74.01	133	15.72	17.39	18.73	19.82	21.39	22.38	23.61	133
N_2O_4	2.54	133	72.84	133	18.52	21.16	23.23	24.86	27.11	28.49	30.16	133
N_2O_5	2.70	133	82.94	133	23.09	26.49	28.97	30.68	32.74	33.81	34.91	133
$CH_2{=}CHNO_2$	...		70.6	178	17.43	21.5	24.9	27.7	31.7	34.5	38.5	178

[a] Estimates. See text.

for estimation of heats of formation of unstable or nonexistent compounds, as well as those of some classes for which no gas-phase data exist. All this information is discussed in the following sections.

The thermodynamic data for these particular compounds are shown in Table XXII.[166–168] The entropy and specific heat values are almost certainly reliable as are most of the heats of formation. A few of these latter, however, require comment. $\Delta H_f^\circ(CH_2N_2)$ is uncertain to ±5 kcal/mole and ΔH_f°(C-$CH_2N{=}N$) may be even less certain. $\Delta H_f^\circ(CH_3CN)$ was obtained by interpolation between $\Delta H_f^\circ(HCN)$ and $\Delta H_f^\circ(C_2H_5CN)$. The series HCN, CH_3CN, and C_2H_5CN is analogous to HCHO, CH_3CHO, C_2H_5CHO, in that both -CN and $>C{=}O$ are very polar groups. Thus, we would expect the increments in ΔH_f° to be the same between analogous pairs in these homologous series. This is approximately the case for $\Delta H_f^\circ(HCN) - \Delta H_f^\circ(HCHO) = 60.0$ kcal/mole and $\Delta H_f^\circ(C_2H_5CN) - \Delta H_f^\circ(C_2H_5CHO) = 58.2$ kcal/mole. Thus, we have used $\Delta H_f^\circ(CH_3CN) - \Delta H_f^\circ(CH_3CHO) = 58.8$ kcal/mole to calculate $\Delta H_f^\circ(CH_3CN)$.

$\Delta H_f^\circ(CH_3NO)$ was obtained from $\Delta H_f^\circ(CH_3)$[163] and $\Delta H_f^\circ(NO)$[133] by assuming $DH^\circ(CH_3NO) = 40$ kcal/mole. The latter value is supported by kinetic evidence from NO-catalyzed isomerization of olefins,[164] although it is not in agreement with an earlier estimate of 57 kcal/mole proposed by Gowenlock, Trotman, and Batt.[179]

J. MISCELLANEOUS COMPOUNDS

There are little or no data on gas-phase heats of formation of 1,1-diamines, azines, Schiff bases, oximes, hydroxylamines, nitroso compounds, nitramines, and azides. However, we have been able to estimate some of these, and our results are shown in terms of the group contributions contained in Table XXXVI. Heats of formation, calculated from this table, are unlikely to be more accurate than ±2 kcal/mole, but are probably not worse. Part of the table is self-explanatory, but the origin of some of the quoted values requires detailed explanation.

Bond dissociation energies can sometimes be useful for estimates of heats of formation, and these have been used to

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(168) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, D. C., 1952.

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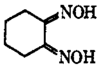
Table XXIII

Heats of Formation of Oximes at 25° and 1 Atm

Oxime	$\Delta H_f°_{cryst}$	*Ref*	t_B, °C	$\Delta H°_{fusion}$ (*estd*)[a]	$\Delta H_v°$(*estd*)[a]	$\Delta H_f°$(*g*)	$\Delta H°$(*g,estd*)
$CH_3CH{=}NOH$	−18.2	168	115	3	10.5	−4.7	−6.3
$CH{=}NOH$ | $CH{=}NOH$	−21.1	168	~280	4	17	0	+1.9
	−81.6	181	~350	4	20	−7.6	−8.1
Octenal 1-monoxime	−56.8	182	~250	4	16.5	−36.3	−36.0
Octenal 2-monoxime	−59.3			4	16.5	−38.8	−38.5
Octenal 3-monoxime	−55.4			4	16.5	−36.9	−37.7
Octenal 4-monoxime	−59.8				16.5	−39.3	−37.7

[a] See text.

obtain the group values for the C-nitroso compounds. It should be pointed out that only the secondary (C–NO) bond strength is known with any assurance, but it would be surprising if other C–NO bond strengths were significantly different. We have, however, made small adjustments to reflect reasonable differences in these bond strengths.

$\Delta H_f°(NH_2OH,g)$ has not been measured directly and the value quoted in the table was obtained by combining the value for $\Delta H_f°(NH_2OH,aq) = -23.5$ kcal/mole[180] with an estimate for the heat of solvation of −14.2 kcal/mole. The latter was obtained by taking the mean of the heats of solvation of N_2H_4 (−14.5 kcal/mole)[168] and H_2O_2 (−13.9 kcal/mole).[168] This procedure offers the most reasonable method of allowing for solvent interaction in hydroxylamine solution.

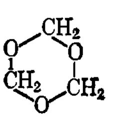
The heats of formation of C-methyl- and O-methylhydroxylamines have never been measured but have been estimated here by consideration of the effects of substituting a methyl group for hydrogen among a series of isoelectronic molecules. The following table for $\Delta H_f°(CH_3XY) - \Delta H_f°(HXY)$ summarizes these numbers (in kcal/mole). All values for $\Delta H_f°$ used in compiling this table are observed values listed in this paper and sections III and IV, except that for $\Delta H_f°(CH_3OOH)$, which is a group additivity value of −30.9 kcal/mole and is probably slightly more reliable. If the figures in parentheses are omitted, trends can nevertheless be seen both across the rows and down the columns of this table, and the two figures in parentheses were inserted to be consistent with these trends. From these two values, $\Delta H_f°(CH_3NHOH)$ and $\Delta H_f°(NH_2OCH_3)$ were obtained.

	X		
Y	*-CH₂-*	*-NH-*	*-O-*
$-CH_3$	−4.6	+1.0	+4.1
$-NH_2$	−5.5	−0.5	(+3.1)[a]
-OH	−8.1	(−2.7)[a]	+1.6

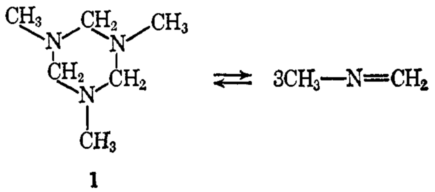
[a] Obtained by interpolation.

Heats of formation of several solid oximes are known from combustion measurements, and these are listed in Table XXIII.[181,182] Unfortunately, their heats of sublimation are not known with any assurance. Attempts to measure these latter have usually been performed by the effusion technique. However, in most cases no checks were made to discover whether the vapors emerging from the effusion cell were actually those of the oximes, or those of their decomposition fragments. If, as we suspect, the latter was often the case, then serious underestimates of heats of sublimation have been made. Thus, we have disregarded quoted values for heats of sublimation and attempted to estimate them. Our estimates are shown in columns 4 and 5 of Table XXIII. The heats of fusion are typical of organic solids of relatively high molecular weight, while the heats of vaporization were derived from Trouton's rule (S_T = 23 eu) and the boiling points (some of which were guessed), as listed in the table. This procedure is admittedly rather crude, but the comparison between $\Delta H_f°$(g) derived from this procedure, and $\Delta H_f°$(g,estd) derived from the group value, N_I–(OH) in Table XXXVI, indicates that the scatter is less than ±2 kcal/mole. Thus, only if all the values of $\Delta H_f°$(g) are systematically in error is the oxime group value for $\Delta H_f°$ worse than ±2 kcal/mole.

In Table XXXVI the group contribution of $C{-}(N)_2(H)_2$ to $\Delta H_f°$ has been derived from the symmetrical triazine shown. The other groups occurring in this ring are all known and the ring strain has been taken by analogy with



as +2.8 kcal/mole. In any case, since the group of interest occurs three times in the molecule, errors in estimation of the ring strain will be reduced by a factor of 3 in the group value. For this reason the value ought to be reasonably reliable. The heat of formation of 1,3,5-trimethylhexahydro-1,3,5-triazine has been derived from measurements of the equilibrium constant for



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in the temperature range 98–164°, by Gowenlock and

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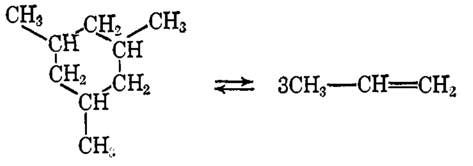
(180) "Selected Values of Chemical Thermodynamic Properties, Series I," Technical Note 270-1, National Bureau of Standards, Washington, D. C., 1965.

(181) C. R. Brent, *Dissertation Abstr.*, **24**, 3108 (1964).

(182) G. Geiseler, M. Rätzsch, K. Ebster, and E. Zeigel, *Ber. Bunsenges. Physik. Chem.*, **70**, 221 (1966).

Thomas.[183] Unfortunately, in their paper, there is an error where by K_{eq} has been wrongly described as K_p but, from examination of the results, it is evidently K_c. Consequently, a quoted value for ΔH° at 35 kcal/mole is, in reality, a value for ΔE°. We have recast their results in the proper units where we find that $\Delta H^\circ = 36.6$ kcal/mole and also that $\Delta S^\circ = 83.5$ eu (at ~400°K). However, there is a more serious criticism of these results, which becomes evident when they are compared with the one for the similar equilibrium



Using group values in section III, we calculate that at 400°K, $\Delta S^\circ \simeq 99$ eu for this system. It has been clearly demonstrated[184] that substitutions of -N< for -CH< in such molecules scarcely affect entropy values, at or near to room temperature. Moreover, where entropy changes are concerned, any small differences between the above equilibrium and that studied by Gowenlock and Thomas ought to be self-cancelling. Therefore, we would expect that in the former equilibrium ΔS° ought to be $\simeq 99$ eu, also. This argument throws some doubt onto what Gowenlock and Thomas were actually observing. Since they, unfortunately, only made pressure measurements, they could not be certain that side reactions were not occurring. We have taken the point of view that while the observed variation of K_p with temperature may be somewhat in error, the over-all magnitude of K_p in the middle of their temperature range (400°K) is approximately correct. With this assumption, and a value of $\Delta S^\circ \simeq 99$ eu, it can be shown that $\Delta H^\circ = 42.8$ kcal/mole (at 400°K). Furthermore, this value is not particularly sensitive to errors in K_p, since an error of a factor of 10 in the latter would only lead to an error of $\simeq 1.8$ kcal/mole in ΔH°. At room temperature, $\Delta H^\circ = 42.5$ kcal/mole, and when combined with a group additivity estimate of $\Delta H_f^\circ(CH_3\text{-}N{=}CH_2) = 17.3$ kcal/mole (which may be obtained directly from Table XXXV), $\Delta H_f^\circ(1) = 9.4$ kcal/mole is obtained.

This section prepared by S. W. Benson and R. Walsh.

VI. Halogen-Containing Compounds

The data for halogen-containing groups, as for the nitrogen groups, come principally from compounds containing no other type of substituent, and conformational corrections differ from those applicable to hydrocarbons. Analysis of the rotational isomers of *n*-propyl chloride,[185,186] bromide,[186] and fluoride,[187] for example, has indicated that the *gauche* isomer is somewhat more stable (~0.1 kcal/mole) than the *trans* isomer. Consequently, no correction for *gauche* interactions between alkyl substituents and halogens will be used. Similarly, no correction will be made for *gauche* interactions between halogens and amino, alkoxy, thiol, and vinyl substituents. On the other hand, analysis of the 1,2-dihaloethanes of chlorine,[188,189] bromine,[181] and fluorine[190] indicates a value +1.0 kcal/mole for chlorine–chlorine and bromine–bromine *gauche* interactions, but none for fluorine–fluorine. We shall adopt a correction of 1.0 kcal/mole for *gauche* interactions between chlorine, bromine, and iodine, and no correction for interactions between halogens and fluorine.[191] Little evidence is available with respect to *cis* corrections in olefins. The *cis* isomer of 1,2-dichloroethylene is 0.4 kcal/mole more stable than the *trans*.[192] We will assume no *cis* correction is necessary for halogens or for halogen–alkyl groups and make the usual assumption that *cis*-alkyl groups are 1.0 kcal/mole less stable than *trans*, including perhaloalkyl groups.[193] Ring strains are assumed to be the same as for the unsubstituted rings. This is probably in error for cyclopropane rings. *ortho* corrections are made as indicated by the data.

Data and Estimated Values. The group values for haloalkanes are summarized in Table XXXVII and a comparison with observed data, from which the groups were obtained, is made in Table XXIV. The values for haloalkenes, -alkynes, and -arenes are given in Table XXXVII and compared with experiment in Table XXV. The heats of formation of all fluorine-substituted compounds have been corrected to conform with $\Delta H_f^\circ{}_{298}(\mathrm{HF,g}) = -64.8$ kcal/mole,[133] and extensive use has been made of Stull's compilation of vapor pressure data[194] to determine $\Delta H_v^\circ(25^\circ)$, when necessary.

Although the data for haloalkanes is somewhat sparse, the estimates agree to ±2 kcal/mole in ΔH_f, ±1 gibbs/mole in S°_{298}, and ±0.5 gibbs/mole in C_p°. Kolesov, *et al.*,[195] have reported $\Delta H_f^\circ{}_{298}(CF_3CH_3) = -175.9$ kcal/mole, 8 kcal/mole more stable than predicted by groups; however, they experienced incomplete combustion (~95%) and only analyzed for HF and CO_2. Formation of $CF_2{=}CH_2$, CO, CH_2F_2, etc., would all lead to low values of ΔH_f, so that their results are not included. Rodgers[196] has suggested that nearest-neighbor interactions only may prove insufficient to adequately predict ΔH_f° of mixed fluorocarbon–hydrocarbon compounds, and there appears adequate evidence of this in haloalkenes. Thus, $CF_2{=}CH_2$ and $CH_2{=}CCl_2$ are 9.3 and 3.9 kcal/mole more stable than the estimates from group contributions (Table XXV). Compounds composed of groups of widely different polarity may show deviations resulting from dipole–dipole interactions. Such an effect might be expected to stabilize $CF_3\text{-}CH_3$ also. Additional evidence of discrepancies in the alkene groups comes from the equilibrium data of Schlag and Peatman[197] (1) and Chesick[198] (2):

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Table XXIV: **Haloalkanes**

	$\Delta H_f°$					$S°$				$C_p°_{300}$			$C_p°_{800}$			
Compound	*Obsd*	*Estd*	Δ	*Ref*	*n*, *σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
CF_3CCl_3	...				3^2	86.4	88.5	−2.0	199	28.1	29.0	−0.9	39.6	39.9	−0.3	199
CF_2ClCF_2Cl	−212.6	−212.6	[0][a]	196	2	...				28.9	27.4	+1.5	...			200
CF_3CF_3	−316.8	−316.8	0.0	133	$3^2 \times 2$	79.4	79.3	0.1	201	25.5	25.4	0.1	38.3	38.6	0.3	201
CCl_3CCl_3	−35.3	−35.4	[0]	196	$3^2 \times 2$	94.8	95.1	0.3	202	32.7	32.6	0.1	41.3	41.2	0.1	202
CBr_3CBr_3	...				$3^2 \times 2$	105.6	105.6	[0]	202	33.4	33.4	[0]	39.9	39.8	[0]	202
$CF_3CHClBr$	...				2×3	87.1	87.1	[0]	203	25.1	25.1	[0]	37.2	37.2	[0]	203
CF_3CHCl_2	...				3	84.1	84.0	0.1	199	24.4	24.8	−0.4	37.3	37.6	−0.3	199
CF_3CH_2Cl	...				3	78.2	78.1	0.1	204	21.4	21.6	−0.2	34.8	34.6	−0.2	204
CF_3CH_2Br	...				3	80.7	81.1	−0.4	204	21.8	21.8	0.0	35.1	34.8	0.3	204
CF_3CH_2I	...				3	82.5	82.8	−0.3	204	21.9	21.9	[0]	35.1	35.1	[0]	204
CF_3CH_2F	...				3	76.0	75.7	0.3	204	20.9	20.8	0.1	34.5	34.5	0.0	204
CF_3CH_3					3^2	68.5	68.5	0.0	205	18.9	18.9	0.0	...			206
CHF_2CH_2F	(−159.5)	−161.1	+1.6	196												
$CHCl_2CH_2Cl$	...				1	80.6	81.5	−0.9	208	21.3	21.0	0.3	33.3	33.2	0.1	208
CH_3CCl_3	...				3^2	77.2	76.4	0.8	209	22.4	22.5	−0.1	33.3	33.6	−0.3	209
CH_3CHF_2	(−121)	−119.4	−1.6	196	3	67.3	67.3	[0]	210	16.1	16.1	[0]	...			210
CH_3CHCl_2	(−31)	−29	[0][c]	211	3	72.9	71.9	1.0	212	18.2	18.3	−0.1	30.9	30.9	0.0	212
CH_2ClCH_2Cl	−31.1	−31.4	0.3	213, 214		...				...			...			
CH_3CH_2F	...				3	63.3	63.6	−0.3	215	14.1	14.3	−0.2	...			215
CH_3CH_2Cl	−25.7	−25.8	0.1	216	3	66.1	66.0	0.1	217	15.1	15.1	0.0	28.3	28.3	0.0	217
CH_3CH_2Br	−14.8	−15.6	0.8	216	3	68.6	69.0	−0.4	217	15.5	15.3	0.2	28.6	28.5	0.1	217
$CF_2ClCF_2CF_2Cl$	...					97.3	97.4	[0]	218	37.4	37.3	[0]	...	...	...	218
$CF_3CF_2CH_3$					3^2	86.3	86.3	[0]	218	28.8	28.8	[0]	...			218
$CH_3CH_2CH_2F$	−66.8	−66.8	[0]	207		...				...			...			218
CH_3CHFCH_3	−68.6	−68.6	[0]	207		...				...			...			...
$CH_3CH_2CH_2Cl$	−31.2	−30.9	−0.3	216		76.4	75.4	1.0	217	20.3	20.6	−0.3	39.2	39.4	−0.2	217
$CH_3CHClCH_3$	−32.9	−33.0	[0]	216	3^2	74.1	74.1	[0]	219	21.3	21.3	[0]	...			219
$CH_3CCl_2CH_3$	(−41.7)	−39.7	[0][c]	211		...				...						
$CH_3CH_2CH_2Br$	−19.9	−20.6	0.7	216		79.2	78.4	0.8	217	20.7	20.8	−0.1	39.4	39.6	−0.2	217
$CH_3CHBrCH_3$	−22.7	−23.6	0.9	216		...				...			...			
$CH_3CH_2CHBrCH_2Br$	−24.4	−23.8	−0.6	220		...				...			...			
$(CH_3)_3CCl$	−43.0	−43.0	[0]	219	3^4	77.0	77.0	[0]	219	27.9	27.9	[0]	...			219
$CH_3CH_2CHBrCH_3$	−28.7	−28.6	−0.1	220, 221		...				...			...			
$CH_3CH_2CH_2CH_2Br$	−25.7	−25.5	−0.2	220		...				...			...			
$CH_3CH_2CH_2CH_2CH_2Br$	−31.0	−30.5	−0.5	220		...				...			...			
n-C_7F_{16}	−801.9	−801.8	0.1	222						...			...			
$CF_3CC_6F_{11}$	−687.3	−687.3[d]	0.0	222												
$CF_3CF_2CC_6F_{11}$	−783.5	−783.5[d]	0.0	222												
1,2-$Br_2CC_6H_{10}$	−26.3	−26.6[d]	0.3	220												
n-$C_6H_{13}Br$	−35.9	−35.5	−0.4	220												
n-$C_7H_{15}Br$	−40.7	−40.5	−0.2	220												
n-$C_8H_{17}Br$	−46.3	−45.5	−0.8	220												
$CH_2ICH_{22}I$	15.9	15.9	[0]	224	2	83.3	83.6	−0.3	224	19.2	18.4	0.8				224
CH_2ICHCH_2I	10.6	10.95	−0.35	224												
CH_3CHICH_2I	8.6	8.6	[0]	224	2, 3	94.3	94.3	[0]	224	(24.1)	24.1	[0]				224
$(CH_3)_3CI$	−17.2	−17.2	[0]	225	3^4	82.5	82.5	[0]	225							
$(CH_3)_2CHCH_2CH(NF_2)CH_2(NF_2)$	−52.0	−52.0	[0]	223												

[a] [0] indicates group value determined by these data. [b] Parentheses indicate questionable data. [c] $\Delta H_f°$'s from ref 211 are generally 2 ± 2 kcal/mole too stable, and group values have been correspondingly adjusted. [d] Calculated assuming strain-free ring.

Table XXV: **Haloalkenes, Alkynes, and Arenes**

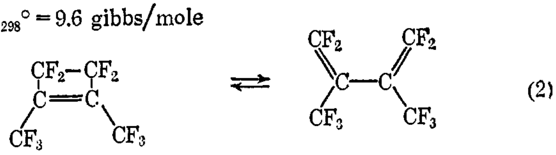
Compound	$\Delta H_f°$ *Obsd*	$\Delta H_f°$ *Estd*	Δ	*Ref*	*n, σ*	*S°* *Obsd*	*S°* *Estd*	Δ	*Ref*	$C_p°_{300}$ *Obsd*	$C_p°_{300}$ *Estd*	Δ	$C_p°_{800}$ *Obsd*	$C_p°_{800}$ *Estd*	Δ	*Ref*
$CFCl{=}CCl_2$					1	81.7	81.9	−0.2	226	21.8	21.7	0.1	28.8	28.8	0.0	226
$CF_2{=}CClBr$					1	82.4	82.4	[0]	227	21.8	21.8	[0]	28.5	28.5	[0]	227
$CFCl{=}CFCl$					2	78.2	78.2	0.0	226	21.0	20.6	0.4	28.4	28.4	0.0	226
$CF_2{=}CBr_2$					2	87.0	83.5	3.5	228	22.2	22.0	0.2	...			
$CF_2{=}CFCl$					1	77.0	77.1	−0.1	229	20.0	20.0	0	28.0	28.0	0.0	229
$CF_2{=}CFBr$					1	79.8	79.8	[0]	230	20.5	20.5	[0]	28.1	28.1	[0]	230
$CF_2{=}CF_2$	−155.0	−155.0	[0]	231	2^2	71.7	71.8	−0.1	231	19.3	19.4	−0.1	27.6	27.6	0.0	231
$CCl_2{=}CCl_2$	−3.6	−3.6	[0]	196	2^2	81.3	81.4	−0.1	232	22.7	22.8	−0.1	29.2	29.2	0.0	232
$CBr_2{=}CBr_2$					2^2	92.4	92.4	0.0	232	24.5	24.6	−0.1	29.7	29.8	−0.1	232
$CHF{=}CCl$					1	75.1	74.9	0.2	233	18.3	18.2	0.1	26.5	26.4	0.1	233
$CF_2{=}CHBr$					1	75.2	75.6	−0.4	234	17.6	17.8	−0.2	26.2	26.2	0.0	234
$CF_2{=}CHF$	−115.1	−115.1	[0]	235	1	69.9	70.1	−0.2	236	16.5	16.5	0.0	25.6	25.6	0.0	236
$CHCl{=}CCl_2$					1	77.6	77.5	0.1	237	19.3	19.3	0.0	26.9	26.9	0.0	237
$CHBr{=}CBr_2$					1	85.7	85.9	−0.2	238	20.5	20.4	0.1	...			238
$CH_2{=}CFCl$					1	67.6	67.4	0.2	239	15.3	15.4	−0.1	24.4	24.3	0.1	239
$CH_2{=}CF_2$	−80.8	−71.5	−9.3	235		...				...			...			
$CH_2{=}CCl_2$	0.3	4.2	−3.9	240	2	69.0	68.3	0.7	241	16.1	16.5	0.4	24.7	24.7	0.0	241
$CHCl{=}CHCl$ (av)					2	69.3	69.4	−0.1	192	15.8	15.8	0.0	24.6	24.6	0.0	192
$CHBr{=}CHBr$ *cis*					2	75.8	75.2	0.6	238	16.5	16.2	0.3	...			238
$CH_2{=}CHCl$	8.1	8.1	[0]	242	1	63.2	63.0	0.2	243, 244	12.9	13.0	−0.1	22.4	22.4	0.0	243, 244
$CH_2{=}CHBr$	18.7	18.7	[0]	245	1	66.0	65.9	0.1	243, 244	13.4	13.2	0.2	22.5	22.5	0.0	243, 244
$CH_2{=}CHI$					1	68.1	68.1	[0]	244	13.9	13.9	[0]	22.7	22.7	[0]	244
$CH_3C{\equiv}CCl$					3	68.0	68.0	[0]	246	17.2	17.2	[0]	27.0	27.0	[0]	246
$CH_3C{\equiv}CBr$					3	70.7	70.7	[0]	246	17.6	17.6	[0]	27.1	27.1	[0]	246
$CH_3C{\equiv}CI$					3	72.4	72.4	[0]	246	17.8	17.8	[0]	27.2	27.2	[0]	246
C_6H_5F	−27.1	−26.3	−0.8	247	2	72.4	72.2	0.4	248	22.7	22.5	0.2	47.6	47.5	0.1	248
o-$C_6H_4F_2$	−68.9	−67.4	−1.5	249	2	77.3	77.0	0.3	250, 251	25.6	25.6	0.0	49.5	49.8	−0.3	251
m-$C_6H_4F_2$	−72.6	−72.4	−0.2	249	2	76.7	77.0	−0.3	251	25.5	25.6	−0.1	49.7	49.8	−0.1	251
p-$C_6H_4F_2$	−71.9	−72.4	0.5	249	2^2	75.6	75.6	0.0	251	25.7	25.6	0.1	49.7	49.8	−0.1	251
p-$FC_6H_4CH_3$	−34.6	−34.2	−0.4	252	3 × 2	81.3	81.4	−0.1	252	27.9	28.2	−0.3	58.6	58.1	0.5	252
$C_6H_5CF_3$	−140.7	−140.7	[0]	253	3 × 2	89.2	89.2	[0]	253	31.4	31.4	[0]	62.8	62.8	[0]	253
4,4-$FC_6H_4C_6H_4F$	−47.7	−48.7	1.0	254												
2,2′-$FC_6H_4C_6H_4F$	−46.6	−47.5	0.9	254												
C_6H_5Cl	12.5	12.7	−0.2	255	2	75.2	75.2	[0]	248	23.6	23.6	[0]	47.9	47.9	[0]	248
o-$C_6H_4Cl_2$	7.1	7.8	−0.7	240, 255												
m-$C_6H_4Cl_2$	5.9	5.6	−0.3	255												
o-ClC_6H_4Et	−1.6	0.5	−2.1	255												
p-ClC_6H_4Et	−1.5	−0.1	−1.4	255												
2,5′-$Cl_2C_6H_3CH{=}CH_2$	21.4	21.6	−0.2	240												
2,2′-$ClC_6H_4C_6H_4Cl$	30.4	30.5	−0.1	254												
4,4′-$ClC_6H_4C_6H_4Cl$	28.8	29.3	−0.5	254												
C_6H_5Br	27.2	27.2	[0]	256		77.9	77.9	[0]	248	24.0	24.0	[0]	48.0	48.0	[0]	248
$C_6H_5CH_2Br$	15.1	15.1	[0]	257												
C_6H_5I	40.5	40.5	[0]	258, 259		80.0	80.0	[0]	248	24.2	24.2	[0]	48.0	48.0	[0]	248
$C_6H_5CH_2I$	30.4	30.4	[0]	260												
C_6F_6	−224.0	−226.8	2.8	261												
C_6Cl_6	−8.3	−9.6	1.3	240												


(1)

I

$\Delta H_{298}° = 11.7$ kcal/mole

$\Delta S_{298}° = 9.6$ gibbs/mole


(2)

II

$\Delta H_{298}° = 0.4$ kcal/mole

$\Delta S_{298}° = 4.9$ gibbs/mole

Writing equilibria 1 and 2 into group notation and subtracting yields

$$[\Delta(1) - \Delta(2)]/2 = [C_d(C_d)(F)\text{–}C_d(C)(F)] - [C_d(C_d)(C) - C_d(C)_2] \quad (3)$$

where we have assumed identical ring strains. Both quantities in brackets on the right-hand side (rhs) of eq 3 are expected to be approximately equal, *i.e.*, rhs(3) $\cong$ 0. This is true for hydrocarbons (H replaces F in eq 3 for which rhs(3) = −0.15 kcal/mole from enthalpies and +0.3 gibbs/mole from entropies. Equilibria 1 and 2, however, yield rhs(3) = 5.2 kcal/mole and 2.35 gibbs/mole for enthalpies and entropies, respectively. These large differences are hard to rationalize with group additivity.

As a result of the above-mentioned contradictions in group additivity for haloalkenes, we feel that the group contributions to $\Delta H°_{298}$ for these compounds should be used with caution, particularly when combining groups with large differences in polarity. Estimates of $S°_{298}$ and $C_p°$, on the other hand, are seen in Table XXV to be accurate to ±1.0 and ±0.5 gibbs/mole, respectively.

The estimates of $\Delta H_f°_{298}$, $S°_{298}$, and $C_p°$ for haloarenes are found accurate to ±2.0 kcal/mole, ±1.0 gibbs/mole, and ±0.5 gibbs/mole, respectively.

This section prepared by S. W. Benson and A. S. Rodgers.

VII. Sulfur, Boron, Phosphorus Compounds and Organometallic Compounds

This section extends the group additivity rules to include organometallic (Sn, Hg, Zn, Cd, Ge, Al, Pb, Ti, V, and Cr) and organononmetallic (S, B, P) compounds. Table XXXVIII lists the best group values and ring corrections. The group values in the table are based on the most stable conformation. We found *gauche* corrections only necessary for the organoboron compounds. In fact, organosulfur compounds indicate no *gauche* interactions. This suggests that these conformational interactions are only important for the first-row elements.

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This reduction in next-nearest-neighbor interaction is coincident with a 20–30% increase in the bonding distance. Bond lengths in ångströms for the first- and second-row elements are, respectively, C–B, 1.56; C–C, 1.54; C–N, 1.47; C–O, 1.47; C–F, 1.38; and C–Al, 1.92; C–Si, 1.87; C–P, 1.87; C–S, 1.82; C–Cl, 1.77.

The utilization of these group values is not restricted solely to the obvious predicting of thermochemical properties of unmeasured compounds. The concept of group additivity of molecular properties allows a check of the internal consistency of the measured thermochemical data of related compounds. This is a plausible test of the reliability of the experimental thermochemical data. As an example, the inconsistencies in the gaseous heat of formation of organosilicon compounds are made apparent by the failure to construct a reproducible set of group values. This inconsistency is evident in the values of the groups [C–(Si)(C)(H)$_2$] − [C–(Si)(H)$_3$] and [Si–(C)(H)$_3$] + [C–(Si)(C)(H)$_2$]. The former group has the values: +18.08 kcal/mole in $Si(CH_3)_4$ − $Si(C_2H_5)_4$; +17.08 kcal/mole in $SiH(CH_3)_3$ − $SiH(C_2H_5)_3$; +12.58 kcal/mole in $SiH_2(CH_3)_2$ − $SiH_2(C_2H_5)_2$; +13.90 kcal/mole in SiH_3CH_3 − $SiH_3C_2H_5$; and the latter group has the values: −17.92 kcal/mole in $C_2H_5SiH_3$; −8.94 kcal/mole in $(CH_3)_2CHCH_2SiH_3$; −11.02 kcal/mole in $CH_3(CH_2)_3SiH_3$. Similarly, a correlation of the heat of formation of $(CH_3)_4M$ and $(C_2H_5)_4M$ and $(C_2H_5)_4M$ compounds, where M = Si, Ge, Sn, Pb, by Telnoi and Rabinovitch[262] demonstrates that the heat of formation of tetramethylsilicon is incorrect.[262a] O'Neal and King[263] found cases where the reported thermochemical data of the organosilicon compounds deviated appreciably from the less stringent bond additivity rule. They concluded that large errors in the heat of combustion are not unusual, and additional thermochemical data of greater accuracy are needed.

A. ORGANOSULFUR COMPOUNDS

1. *Alkylthiols*

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p{}^\circ{}_{300}$ are ±0.2 kcal/mole, ±0.2 eu, and ±0.1 gibbs/mole, respectively. The uncertainty in the heat capacity at high temperatures (800°K) increases to ±0.5 gibbs/mole.

2. *Thiaalkanes*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p{}^\circ{}_{300}$ are ±0.3 kcal/mole, ±0.2 eu, and ±0.3 gibbs/mole, respectively. The uncertainty in the heat capacity at high temperatures (800°K) increases to ±0.5 gibbs/mole. The disagreement between calculated and observed values of $S^\circ{}_{298}$ and $C_p{}^\circ{}_{300}$ for the compound $(CH_3)_2CHSCH(CH_3)_2$ (see Table XXVI[264–279]) suggests that there is an error in the observed values.

3. *Aromatic Sulfides*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ is ±0.3 kcal/mole.

4. *Thiaalkanes*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ is ±0.2 kcal/mole.

5. *Dithiaalkanes*

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p{}^\circ{}_{300}$ are ±0.5 kcal/mole, ±0.4 eu, and ±0.2 gibbs/mole, respectively. At higher temperatures (800°K), the uncertainty in the heat capacity increases to ±0.7 gibbs/mole.

6. *Sulfoxides*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ is ±1.0 kcal/mole. This is larger than the reported experimental precision, suggesting systematic errors.

7. *Sulfones*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ is ±2.0 kcal/mole for aliphatic, ±2.8 kcal/mole for alkene, and ±1.9 kcal/mole for aromatic sulfones. Consequently, the inconsistencies in the heats of formation are considerably larger than the reported experimental precision. The gas-phase heats of formation were derived from the standard heats by combining with the relevant heats of fusion, vaporization, and sublimation. In the case of the sulfones, these latter quantities have been estimated by empirical methods. It is quite possible that the inconsistencies in the group values arise from these crude estimates.

8. *Vinyl Sulfones*

The group additivity rule indicates that the reported heat of formation of *p*-tolylprop-1-ene sulfone (see Table XXVI) is inconsistent with the heats of formation of the other members of the homologous series.

9. *Thiolacetic Acid*

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ is ±0.9 kcal/mole.

10. *Thiophenes and Thiolenes*

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, $C_p{}^\circ{}_{300}$, and $C_p{}^\circ{}_{800}$ for the thiophenes are ±0.1 kcal/mole, ±0.8 eu, ±0.4 gibbs/mole, and 0.6 gibbs/mole, respectively.

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(262a) Expressing the heat of formation of $(CH_3)_4M$ and $(CH_3CH_2)_4M$ in terms of their groups and combining, we find the relation $\Delta H_f{}^\circ[(CH_3CH_2)_4M] = \Delta H_f{}^\circ[(CH_3)_4M] + 4\{[C-(M)(C)(H)_2] - [C-(M)(H)_3] + [C-(C)(H)_3]\}$. If we invoke bond additivity rules, the linear correlation $\Delta H_f{}^\circ[(CH_3CH_2)_4M] = \Delta H_f{}^\circ[(CH_3)_4M]$ + constant is obtained. The error in this relation should not be larger than ± 5 kcal/mole (see ref 2).

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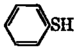
Table XXVI

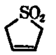
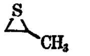
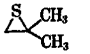
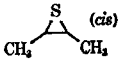
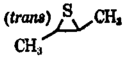
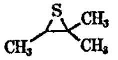
Organosulfur Compounds

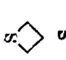
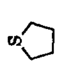
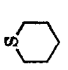
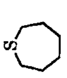
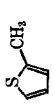
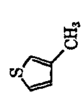
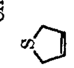
Compound	$\Delta H_f°_{298}$					$S°_{298}$				$C_p°_{300}$			$C_p°_{800}$			
	Obsd	*Estd*	Δ	*Ref*	*n, σ*	*Obsd*	*Estd*	Δ	*Ref*	*Obsd*	*Estd*	Δ	*Obsd*	*Estd*	Δ	*Ref*
CH_3SH	−5.46	−5.46	[0.0]	264	3	60.96	60.96	[0.0]	265	12.05	12.05	[0.0]	20.32	20.32	[0.0]	265
	−5.27		+0.19	265												
CH_3CH_2SH	−10.99	−11.11	+0.12	264	3	70.77	70.84	+0.07	265	17.44	17.43	+0.01	31.83	32.58	−0.75	265
	−10.87		+0.24	265												
$CH_3(CH_2)_2SH$	−16.19	−16.06	−0.13	264	3	80.40	80.26	+0.14	265	22.75	22.93	−0.18	43.60	43.65	−0.05	265
	−16.06		[0.0]	265												
$CH_3(CH_2)_3SH$	−21.02	−21.01	−0.01	264	3	89.38	89.68	[0.0]	265	28.37	28.43	−0.06	55.68	54.72	+0.96	265
	−20.89		+0.12	265												
$CH_3(CH_2)_4SH$	−25.88	−25.96	+0.08	264												
	−26.70		−0.74		3	99.28	99.10	+0.18	295	33.91	33.93	−0.02	66.78	65.79	+0.99	268
	−25.94		+0.02	269												
$CH_3(CH_2)_5SH$	−30.82	−30.91	+0.09	269	...											
$CH_3(CH_2)_6SH$	−35.65	−35.86	+0.21	269	...											
$CH_3(CH_2)_9SH$	−50.57	−50.71	+0.14	269	...											
$((CH_3)_2CH)SH$	−18.19	−18.18	−0.01	264	3^2	77.51	77.88	−0.37	264	23.04	23.09	−0.05	43.26	43.24	+0.02	264
$(CH_3)_2CH\ CH_2SH$	−23.21	−23.09	−0.12	264	3^2	86.73	87.01	−0.28	264	28.41	28.16	+0.25	53.77	54.91	−1.14	264
$(CH_3)(CH_3CH_2)CHSH$	−23.12	−23.13	+0.01	264	3^2	87.65	87.30	+0.35	267	28.64	28.59	+0.05	54.29	54.31	−0.02	264
$(CH_3)_3CSH$	−26.14	−26.17	+0.03	264	3^4	80.79	80.83	−0.04	264	29.04	29.00	+0.04	55.53	55.08	+0.45	264
						80.78		−0.05		29.05		+0.05	54.36		−0.72	
$(CH_3)_2CH(CH_2)_2SH$	−27.41	28.04	−0.63	264	...											
$(CH_3)_2(CH_3CH_2)CSH$	−30.34	−31.12	+0.78	264	3^4	92.48	92.43	+0.05	264	34.46	34.50	−0.04	66.28	66.15	+0.13	264
$HS(CH_2)_2SH$	−2.23	−2.06	−0.17	266	...									...		...
$HS(CH_2)_3SH$	−7.03	−7.01	−0.02	266	...									...		...
$HS(CH_2)_4SH$	−12.03	−11.96	−0.07	266	...				...					...		...
$HS(CH_2)_5SH$	−16.87	−16.91	+0.04	266	...				... ...					...		...
SH	−11.42	−11.52	+0.10	264	...	86.38	86.39	−0.01	264	25.94	25.21	+0.73	58.61	58.55	+0.06	264
SH	−22.90	−22.77	−0.13	264	...	87.37	87.31	+0.06	267	32.13	31.81	+0.32	75.19	73.37	+1.82	267
	−22.85		−0.08	294												
SH	26.66	26.66	[0.0]	264	...	80.51	80.51	[0.0]	264	25.22	25.22	[0.0]	51.59	51.59	[0.0]	264
CH_2SH	21.9	21.90	[0.0]	264	...				...							... ...
$(CH_3)_2S$	−8.94	−8.65	−0.29	264, 265	$3^2 \times 2$	68.32	68.25	+0.07	264, 265	17.77	17.37	+0.40	31.59	31.45	+0.14	264, 265
$CH_3CH_2S_3CH$	−14.22	−14.30	+0.08	264, 265	3^2	79.62	79.50	+0.12	264, 265	22.82	22.75	+0.07	42.93	43.71	+0.78	264.265
$CH_3S(CH_2)_2CH_3$	−19.51	−19.25	−0.26	264, 265	3^2	88.84	88.92	−0.08	264, 265	28.17	28.26	−0.09	54.45	54.78	−0.33	264, 265
$(CH_3)_2CHSCH_3$	−21.58	−21.37	−0.21	264, 265	3^3	85.87	86.52	−0.65	264, 265	28.82	28.41	+0.41	54.89	54.37	−0.52	264, 265
$CH_3S(CH_2)_3CH_3$	−24.39	−24.20	−0.19	264, 265	3^2	98.43	98.34	+0.09	264, 265	33.79	33.75	+0.04	66.53	65.85	+0.68	264, 265
	−24.20		[0.0]													
$CH_3SC(CH_3)_3$	−28.93	−29.36	+0.43	264, 265	3^5	89.21	89.49	−0.28	264, 265	34.66	34.22	+0.44	66.74	66.21	+0.53	264, 265
$CH_3S(CH_2)_4CH_3$	−29.10	−29.15	+0.05	264, 265	...				...							...
$CH_3CH_2SCH_2CH_3$	−19.92	−19.95	+0.03	264, 265	$3^2 \times 2$	87.96	88.01	−0.05	264, 265	28.09	28.13	−0.04	54.91	55.97	−1.06	264, 265

$CH_3CH_2SCH_2CH_2CH_3$	−24.97	−24.90	−0.07	264, 265	3^2	98.97	98.80	−0.17	264, 265	33.40	33.63	−0.23	66.68	67.04	−0.36	264, 265
$(CH_3)_2CHSCH_2CH_3$	−28.0	−27.02	+0.98	264, 265	...				...							...
$CH_3CH_2S(CH_2)_3CH_3$	−30.3	−29.85	+0.45	264, 265	...				...							...
$(CH_3)_3CSCH_2CH_3$	−35.3	−35.01	+0.29	264, 265	...				...							...
$CH_3(CH_2)_2S(CH_2)_2CH_3$	−29.74	−29.85	+0.11	264, 265	$3^2 \times 2$	107.22	106.55	+0.67	264, 265	38.71	39.13	−0.42	78.45	78.11	+0.34	264, 265
	−29.93		−0.08													
$(CH_3)_2CHSCH(CH_3)_2$	−33.84	−34.09	+0.25	264, 265	$3^4 \times 2$	99.56	102.08	−2.52	264, 265	40.65	39.45	+1.20	77.12	77.29	+0.17	264, 265
	−34.10		−0.01													
	−33.78		+0.31													
$CH_3(CH_2)_3S(CH_2)_3CH_3$	−39.96	−39.75	−0.21	264, 265	$3^2 \times 2$	125.84	125.69	+0.15	264, 265	49.70	50.13	−0.43	100.58	100.25	+0.33	264, 265
$(CH_3)_2CHCH_2SCH_2CH(CH_3)_2$	−42.9	−43.91	+1.01	264, 265	...				...							...
$(CH_3)_3CSC(CH_3)_3$	−49.6	−50.07	+0.47	264, 265	...				...							...
$CH_3(CH_2)_4S(CH_2)_4CH_3$	−49.0	−49.65	+0.65	264, 265	...				...							...
$((CH_3)_2CH\ CH_2)_2S$	−53.0	−53.81	+0.81	264, 265	...				...							...
$C_6H_5SCH_3$	23.5	23.78	−0.28	264, 265	...				...							...
$C_6H_5CH_2SCH_3$	19.0	18.71	+0.29	264, 265	...				...							...
$C_6H_5SCH_2CH_3$	18.4	18.13	+0.27	264, 265	...				...							...
$C_6H_5CH_2SCH_2CH_3$	12.4	13.06	−0.66	264, 265	...				...							...
$C_6H_5SC_6H_5$	55.3	55.30	[0.0]	264, 265	...				...							...
$C_6H_5CH_2SCH_2C_6H_5$	46.1	46.07	+0.03	264, 265	...				...							...
$CH_2{=}CHCH_2SCH_2CH_3$	4.3	4.18	+0.12	264, 265	...				...							...
$CH_2{=}CHCH_2SC(CH_3)_3$	−11.0	−10.88	−0.12	264, 265	...				...							...
CH_3SSCH_3	−5.71	−6.06	+0.35	270	$3^2 \times 2$	80.46	79.84	+0.62	270	22.61	22.84	−0.23	37.66	36.80	+0.86	270
$CH_3CH_2SSCH_2CH_3$	−17.78	−17.36	−0.42	270	$3^2 \times 2$	99.07	99.60	−0.53	270	33.91	33.60	+0.31	60.19	61.32	−1.13	270
$CH_3(CH_2)_2SS(CH_2)_2CH_3$	−27.78	−27.26	−0.52	270	$3^2 \times 2$	118.30	118.44	−0.14	270	44.50	44.60	−0.10	83.70	83.46	+0.24	270
	−27.95		−0.69													
$CH_3(CH_2)_3SS(CH_2)_3CH_3$	−37.63	−37.16	−0.47	270	...				...							
$((CH_3)_2CHCH_2S)_2$	−40.61	−41.32	+0.71	270	...				...							...
$(CH_3)_3CSSC(CH_3)_3$	−47.05	47.48	+0.43	270	...				...							...
$C_6H_5SSC_6H_5$	58.4	58.40	[0.0]	270	...				...							...
$CH_3(SO)CH_3$	−34.57	−34.57	[0.0]	264, 265	$3^2 \times 2$	73.20	73.20	[0.0]	264, 265	21.26	21.26	[0.0]	37.02	37.02	[0.0]	264, 265
$CH_3CH_2(SO)CH_2CH_3$	−49.0	−50.01	+1.01	264, 265	$3^2 \times 2$											
$CH_3CH_2(SO)C(CH_3)_3$	−65.5	−65.50	[0.0]	264, 265	...				...							...
$CH_3(CH_2)_2(SO)(CH_2)_2CH_3$	−60.9	−59.91	−0.99	264, 265	...				...							...
$CH_2{=}CHCH_2(SO)CH_2CH_3$	−24.7	−24.71	[0.0]	264, 265	...				...							...
$C_6H_5(SO)C_6H_5$	25.6	25.60	[0.0]	264, 265	...				...							...
$CH_3(SO_2)CH_3$	−89.9	−89.90	[0.0]	264, 265	$3^2 \times 2$	76.0	76.0	[0.0]	264, 265	23.9	23.9	[0.0]				264, 265
$CH_3(SO_2)CH_2CH_3$	−98.7	−97.58	−1.12	264, 265	...				...							...
$CH_3(SO_2)(CH_2)_3CH_3$	−110.0	−107.48	−2.52	264, 265	...				...							...
$CH_3(SO_2)(CH(CH_3)_2)$	−104.2	−102.60	−1.60	264, 265	...				...							...
$CH_3(SO_2)C(CH_3)_3$	−112.3	−110.67	−1.63	264, 265	...				...							...
$CH_3CH_2(SO_2)CH_2CH_3$	−103.8	−105.26	+1.46	264, 265	...				...							...
$CH_3CH_2(SO_2)C(CH_3)_3$	−117.6	−118.35	+0.75	264, 265	...				...							...
$(CH_3)_2CH(SO_2)CH(CH_3)_2$	−112.1	−115.30	+3.20	264, 265	...				...							...
$CH_3(CH_2)_3(SO_2)(CH_2)_3CH_3$	−122.2	−125.06	+2.86	264, 265	...				...							...
$((CH_3)_2CHCH_2)_2(SO_2)$	−126.3	−129.22	+2.92	264, 265	...				...							...
$(CH_3)_3C(SO_2)C(CH_3)_3$	−129.7	−131.44	+1.74	264, 265	...				...							...

Table XXVI (Continued)

Organosulfur Compounds

Compound	$\Delta H_f{}^\circ_{298}$					S°_{298}				$C_p{}^\circ_{300}$			$C_p{}^\circ_{800}$			
	Obsd	Estd	Δ	Ref	n, σ	Obsd	Estd	Δ	Ref	Obsd	Estd	Δ	Obsd	Estd	Δ	Ref
$CH_2{=}CHCH_2(SO)_2CH_3$	−73.5	−72.11	−1.39	264, 265	...				...							...
$CH_2{=}CHCH_2(SO_2)CH_2CH_3$	−78.4	−79.79	+1.39	264, 265	...				...							...
$CH_3(SO_2)C_6H_5$	−63.4	−63.57	+0.17	264, 265	...				...							...
$CH_3(SO_2)CH_2C_6H_5$	−68.0	−63.35	−4.65	264, 265	...				...							...
$C_6H_5CH_2(SO_2)CH_2C_6H_5$	−36.8	−36.80	[0.0]	264, 265	...				...							...
$C_6H_5(SO_2)C_6H_5$	−28.7	−30.98	+2.28	264, 265	...											...
$CH_3C_6H_4(SO_2)C_6H_4CH_3$	−49.0	−46.72	−2.28	264, 265	...				...							...
$CH_3C_6H_4(SO_2)CH_3$	−71.6	−71.44	−0.16	264, 265	...				...							...
$C_6H_5(SO_2)(SO_2)C_6H_5$	−114.9	−114.90	[0.0]	264, 265	...				...							...
$CH_2{=}CHSO_2CH{=}CH_2$	−36.0	−36.0	[0.0]	271	...											
$C_6H_5SO_2CH{=}CH_2$	−30.8	−31.0	+0.2	271	...											
$CH_3C_6H_4SO_2CH{=}CH_2$	−38.7	−38.9	+0.2	271	...											
$CH_3C_6H_4SO_2CH{=}CHCH_3$	−49.9	−46.6	−3.3	271	...											
$CH_3C_6H_4SO_2C(CH_3)C_6H_5{=}CH_2$	−47.0	−47.0	[0.0]	271	...											
$CH_3C_6H_4SO_2CH{=}CHC_6H_5$ (*trans*)	−16.5	−16.2	−0.3	271	...											
$CH_3C_6H_4SO_2CH{=}CHC_6H_5$ (*cis*)	−14.3	−15.2	+0.9	271	...											
$C_6H_5SO_2CH{=}CHC_6H_5$	−8.3	−8.3	0.0	271	...											
$((CH_3CH_2)_2N)_2S_2$	−16.8	−16.72	−0.08	277	...				...							...
$((CH_3CH_2)_2N)_2SO_2$	−139.0	−139.0	[0.0]	277	...				...							...
$((CH_3CH_2)_2N)_2SO$	−66.2	−66.28	+0.08	277	...				...							...
$CH_3(CO)SH$	−43.5	−43.05	−0.45	273	...				...							...
	−42.6		+0.45	272	...				...							...
CF_3SH				...	3	69.45	69.45	[0.0]	276							...
NH_2CSNH_2	−6.0	−6.00	[0.0]	264, 265	2	72.44	72.44	[0.0]	264, 265	17.72	17.73	[0.0]	29.06	29.07	[0.0]	264.275
CH_3NCS	+27.1	+27.1	[0.0]	272, 273	3	69.30	69.30	[0.0]	300	15.70	15.70	[0.0]	25.87	25.87	[0.0]	300
S_8	24.35	24.32	[0.0]	274	8	102.76	102.76	[0.0]	274	37.25	37.28	[0.0]	42.62	42.64	[0.0]	274
	−61.1	−61.1	[0]	264, 265	...											
	19.93	19.93	[0]	264, 265	2	61.01	61.01	[0]	264, 265	12.90	12.90	[0]	25.61	25.61	[0]	264, 265
	10.99	12.86	−1.87	264, 265	...				...							...
	2.73	4.87	−2.14	264, 265	...				...							...
	2.73	6.79	−4.06	264, 265	...				...							...
	0.89	5.79	−4.90	264, 265	...				...							...
	−5.09	−1.10	−3.99	264, 265	...				...							...

	14.63	14.63	[0]	264,265	2	68.14	68.14	[0]	264,265	16.66	16.66	[0]	36.40	36.40	[0]	264,265
	−7.57 −8.17 −8.02	−7.96	+0.39 −0.21 −0.06	264 278	2	73.94	73.94	[0]	264,265	21.85	21.85	[0]	47.66	47.66	[0]	264,265
	−14.91 −14.96	−14.64	−0.27 −0.32	264,265	2	77.26	77.26	[0]	264,265	26.03	26.03	[0]	64.00	64.00	[0]	264,26
	−15.7	−15.7	[0]	264,265	. . .				. . .							. . .
	27.82	27.87	0.05	264	2	66.65	67.45	−0.80	264	17.52	17.13	+0.39	36.01	35.53	+0.48	264
	20.16	20.16	[0]	264	3	76.42	76.62	[0]	22.92	22.92	22.66	−0.26	46.43	45.31	−1.12	264
	19.94	19.89	+0.05	264	3	76.79 76.84	76.05	+0.74 +0.79	264 279	22.80 22.94	23.26	−0.46 −0.32	45.95 46.49	46.70	−0.75 −0.21	264 279
	20.86	20.86	[0]	278	. . .				. . .							. . .
	21.78	21.78	[0]	278	. . .				. . .							. . .

11. Thiocycloalkanes

The thermodynamic data for thiocyclopropane are apparently reliable. On the other hand, the methylated thiocycloalkanes (2-methyl, 2,2-dimethyl, *cis*-2,3-dimethyl, *trans*-2,3-dimethyl, and trimethyl) deviate from the additivity rule. Application of the principle of group additivity to thiocyclopropane leads to a ring correction for the standard heat of formation of +19.72 kcal/mole. The ring corrections for 2-methyl-, 2,2-dimethyl-, *cis*-2,3-dimethyl-, *trans*-2,3-dimethyl-, and trimethylth ocyclopropane are +17.85, 17.58, 15.66, 14.82, and 15.73 kcal/mole, respectively (the *cis*-ring correction used for thiocyclopropane was 1.0 kcal/mole, the same as found for cyclopropane). The standard heats of formation in the gas phase of the methylated thiocyclopropanes seem on the average low by 3.4 kcal/mole, relative to thiocyclopropane.

B. ORGANOPHOSPHORUS COMPOUNDS (TABLE XXVII[280])

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$ values (kcal/mole) are as follows: R_3P, ±0.9; $(C_6H_5)_3P$, ±3.6; $(RO)_3P$, ±2.0; $R(PO)X_2$, ±0.9; $R(PO)(OH)_2$, ±1.6; $(R_2N)_3P$, ±1.2; $(R_2N)_3PO$, ±2.5.

In the cyclic phosphorus–nitrogen compounds, the strain energy of the rings is apparently zero. Otherwise, one would expect a difference in the strain energy of the rings $(PNCl_2)_3$ and $(PNCl_2)_4$. The value of the group $P{:}N\text{–}(N{:}P)(Cl)_2(P{:}N)$ derived from these two rings is 58.8 ±0.2 kcal/mole.

The gas-phase standard heats of formation of the compounds $(CH_3)_2CHO(CH_3)(PO)(OH)$, $(CH_3CH_2O)_2(PO)(OH)$, $(CH_3CH_2CH_2CH_2)_3PO$, and $(CH_3CH_2CH_2)_3PO$ were calculated from group values, which were combined with observed heats of reaction to determine the heats of formation of the related compounds, $(CH_3)_2CHO(CH_3)(PO)(Cl)$, $(CH_3CH_2O)_2(PO)F$, $(CH_3CH_2CH_2CH_2)_3P$, and $(CH_3CH_2CH_2)_3P$.

C. ORGANOBORON COMPOUNDS

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$ values (kcal/mole) are as follows: R_3B, ±1.6; RBF_2, ±3.0; $(RO)_2BH$, ±1.1; $(RO)_2BCl$, ±1.2; $(RO)BCl_2$, ±0.7; $(RO)_3B$, ±1.2; $(RS)_3B$, ±2.0; R_3BO_3, ±3.1; $(R_2N)_2BCl$, ±1.3; R_2NBCl_2, ±1.1.

The calculated heat of formation of the alkylborine $((CH_3CH_2)(CH_3)CH)_3B$ deviates from its experimental value by 5.2 kcal/mole (see Table XXVIII[281–288]). Either the observed heat of formation is in considerable error or the correction for next-nearest neighbor interaction is stronger than we have allowed. At present, the evidence is too slight for a decisive conclusion.

Trialkylthioboranes and Triphenylthioboranes. The calculated heat of formation of $(CH_3S)_3B$ deviates from its experimental value by 12.0 kcal/mole (see Table XXVIII), indicating a considerable error in the observed heats of formation. This disparity does not exist in the compounds $(CH_3O)_2BH$ and

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Table XXVII

Organophosphorus Compounds[a]

Compound	$\Delta H_f{}^\circ{}_{298}$ Obsd	$\Delta H_f{}^\circ{}_{298}$ Estd	Δ	$S^\circ{}_{298}$ Obsd	$S^\circ{}_{298}$ Estd	Δ	Ref	n, σ
$(CH_3)_3P$	−23.2	−23.2	[0]					
	−23.0		+0.2					
$(CH_3CH_2)_3P$	−32.8	−30.6	−2.2					
$(C_6H_5)_3P$	72.4	72.4	[0]					
	76.0		+3.6					
$(CH_3O)_3P$	−165.0	−167.5	+2.0					
$(CH_3CH_2O)_3P$	−191.9	−193.0	+1.1					
$((CH_3)_2CHO)_3P$	−221.8	−218.8	−3.0					
$(CH_3)_3PO$	−103.0	−103.0	[0]					
$(CH_3CH_2CH_2)_3PO$		−128.1						
$(CH_3CH_2CH_2)_3P$	−44.9	−45.5	+0.6					
$(CH_3CH_2CH_2CH_2)_3PO$		−141.1						
$(CH_3CH_2CH_2CH_2)_3P$	−59.0	−58.5	−0.5					
$(C_6H_5)_3PO$	3.5	3.5	[0]					
$CH_3(PO)(OCH_2CH_3)_2$	−228.1	−228.1	[0]					
$CH_3CH_2(PO)(OCH(CH_3)_2)_2$	−248.7	−248.7	0					
$(CH_3CH_2O)_3PO$	−282.4	−282.4	[0]					
$((CH_3)_2CHO)_3PO$	−308.2	−308.2	0					
$CH_3(PO)Cl_2$	−133.9	−133.1	−0.8	81.2	81.2	[0]		3
$CH_3(PO)F_2$				75.0	75.0	[0]		3
$CH_3(PO)FCl$				80.4	80.4	[0]		2, 3
$CH_3CH_2(PO)Cl_2$	−135.5	−136.5	+1.0					
$CH_3(PO)(OH)_2$	−241.1	−239.6	−1.5					
$CH_3CH_2(PO)(OH)_2$	−241.4	−243.0	+1.6					
$CH_3CH_2PCl_2$	−62.6	−62.7	+0.1					
$((CH_3)_2CHO)(CH_3)(PO)(OH)$		−242.4						
$((CH_3)_2CHO)(CH_3)(PO)(Cl)$	−190.5	−190.5	[0]					
$(CH_3CH_2O)_2(PO)OH$		−288.2						
$(CH_3CH_2O)_2(PO)F$	−286.3	−286.3	[0]					
$(CH_3CH_2O)_2(PO)O(PO)(OCH_2CH_3)_2$	−500.8	−500.8	[0]					
$(CH_3CH_2O)_2P(OH)$	−209.7	−209.7	[0]					
$((CH_3CH_2)_2N)_3P$	−49.4	−50.5	+1.1					
$((CH_3)_2N)_3P$	−32.0	−30.7	−1.3					
$((CH_3)_2N)_3PO$	−114.1	−111.7	−2.4					
$((CH_3CH_2)_2N)_3PO$	−148.8	−151.3	−2.5					
$(CH_3)_3P{:}N(CH_2CH_3)$	−20.4	−20.4	[0]					
$(C_6H_5)_3P{:}N(CH_2CH_3)$	40.0	40.0	[0]					
$(Cl_2P{:}N)_3$	−175.9	−174.9	−1.3					
$(Cl_2P{:}N)_4$	−231.7	−233.2	+1.1					
$((CH_3)_2P{:}N)_2$	−107.1	−107.1	−0.1					
$((C_6H_{11}O)_2P{:}N)_3$	−565.0	−564.9	−0.1					
$(C_6H_5)_2P{:}N)_4$	58.7	58.8	−0.1					

[a] All data from ref 280.

$((CH_3)_2CHO)_2BH$, which justifies ascribing the disparity in $(CH_3S)_3B$ to experimental error.

D. ORGANOMETALLIC COMPOUNDS

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$ values (kcal/mole) are as follows: R_4Sn, ±1.7; R_3SnX, ±1.6; R_2SnX_2, ±1.2; $RSnX_3$, ±0.7; R_3SnH, ±1.3; $R_3Sn(CH{=}CH_2)$, ±1.4; R_3SnSnR_3, ±2.8.

The group values clearly indicate that an inconsistency exists between the thermochemical data of $(CH_3)_3SnSn(CH_3)_3$ and $(CH_3CH_2)_3SnSn(CH_2CH_3)_3$, suggesting that the heats of formation of the ethyl compounds should be reduced by 16–18 kcal/mole (see Table XXIX[281, 289–296]). This amounts to less than 1% systematic error in the measured heats of combustion, which is entirely possible.

The gas-phase standard heats of formation of the compounds $(CH_3CH_2CH_2CH_2)_3SnCl$ and $(CH_2{=}CH)_4Sn$ were calculated from group values, which were combined with the observed heats of redistribution reaction to obtain the heat of formation of the related compounds, $(CH_3CH_2CH_2CH_2)SnCl_3$ and $(CH_2{=}CH)_3SnCl$.

1. Zinc

The uncertainty in the predicted $\Delta H_f{}^\circ{}_{298}$ of the tetraalkylzinc compounds is ±2.5 kcal/mole.

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Table XXVIII

Organoboron Compounds

Compound	(*gauche*)	$\Delta H_f{}^\circ{}_{298}$ *Obsd*	$\Delta H_f{}^\circ{}_{298}$ *Estd*	Δ	*Ref*
$(CH_3)_3B$	(0)	−29.3	−29.3	[0]	281
$(CH_3CH_2)_3B$	(0)	−36.5	−36.0	−0.5	281
$(CH_3CH_2CH_2CH_2)_3B$	(0)	−67.7	−65.7	−2.0	281
$((CH_3)_2CHCH_2)_3B$	(3)	−66.9	−67.1	+0.2	281
$((CH_3CH_2)(CH_3)CH)_3B$	(9)	−58.7	−63.9	+5.2	281
$(CH_3(CH_2)_4CH_2)_3B$	(0)	−94.8	−95.4	+0.6	281
$(CH_3(CH_2)_5CH_2)_3B$	(0)	−109.4	−110.3	+0.9	281
$(CH_3(CH_2)_6CH_2)_3B$	(0)	−124.5	−125.1	+0.6	281
$(CH_3CH_2CH_2CH_2)_2BCl$	(0)	−86.7	−86.7	[0]	281
$(CH_3CH_2CH_2CH_2)_2BBr$	(0)	−71.3	−71.3	[0]	281
$(CH_3CH_2CH_2CH_2)_2BI$	(0)	−53.3	−53.3	[0]	281
CH_3BF_2	(0)	−199	−203	+4	281
$CH_3CH_2BF_2$	(0)	−209	−205	+4	281
$(CH_3)_2CHBF_2$	(0)	−212	−212	0	281
$CH_2{=}CHBF_2$	(0)	−171	−171	[0]	281
$(CH_3O)_2BH$	(0)	−139.2	−139.2	[0]	283
$((CH_3)_2CHO)_2BH$	(0)	−174.4	−173.3	−1.1	282
$(CH_3CH_2O)_2BCl$	(0)	−197.0	−195.8	−1.2	284
		−195.8[a]		[0]	
$(CH_3CH_2O)BCl_2$	(0)	−149.9	−149.2	−0.7	284
		−149.2[a]		[0]	
$(CH_3CH_2O)_3B$	(0)	−240.8	−239.6	−1.2	281
		−239.6[a]		[0]	
$(CH_3)_3BO_3$	(0)	−215.7	−215.7	[0]	281
$(CH_3CH_2)_3BO_3$	(0)	−240.8	−245.5	+4.7	281
$(CH_3CH_2CH_2)_3BO_3$	(0)	−260.9	−260.4	−0.5	281
$(CH_3CH_2CH_2CH_2)_3BO_3$	(0)	−279.4	−275.2	−4.2	281
$(CH_3CH_2CH_2CH_2)_2BOH$	(0)	−130.6	−130.6	[0]	281
$((CH_3)_2N)_3B$	(0)	−65.9	−65.9	[0]	286
$((CH_3)_2N)_2BCl$	(0)	−85.3	−84.0	−1.3	285
		−84.0[a]		[0]	
$(CH_3)_2NBCl_2$	(0)	−99.1	−98.0	−1.1	285
		−98.0[a]		[0]	
$(CH_3S)_3B$	0	−37.4	−49.4	−12.0	288
$(CH_3CH_2S)_3B$	0	−68.2	−66.4	−1.8	288
$(CH_3CH_2CH_2S)_3B$	0	−80.0	−81.2	−1.2	288
$(CH_3CH_2CH_2CH_2S)_3B$	0	−94.2	−96.2	−2.0	288
$(CH_3CH_2CH_2CH_2CH_2S)_3B$	0	−110.7	−111.1	−0.4	288
$(CS)_3B$	0	45.1	45.1	[0]	288

[a] Heat of vaporization corrected to 25°.

2. *Organotitanium, -vanadium, and -chromium Compounds*

The reported uncertainty in $\Delta H_f{}^\circ{}_{298}$ is about ±2 kcal/mole. Group additivity suggests ±9 kcal/mole for titanium alkoxides. *gauche* corrections were not employed. The deviation of the calculated heat of formation from the observed value could not be reconciled with next-nearest neighbor interactions. Apparently these errors are associated with the experimental values. A comparison of the steric interactions in the titanium alkyl oxides with the observed steric interactions in di-*t*-butyl ether indicates that the intramolecular strain must be nearly zero for these compounds.

In Table XXX it is immediately apparent that the heat of formation of $[(CH_3CH_2)(CH_3)_2CO]_4Ti$ is in error by at least 16 kcal/mole. The other values fall into two sets: $[CH_3CH_2O]_4Ti$, $[(CH_3)_2CHO]_4Ti$, $[CH_3(CH_3CH_2)CHO]_4Ti$, $[(CH_3)_3CO]_4Ti$ with an average value of −251 ± 2 kcal/mole and $[CH_3(CH_2)_2O]_4Ti$, $[CH_3(CH)_2)_3O]_4Ti$, $[CH_3(CH_2)_4O]Ti$, $[(CH_3)_2CHCH_2O]_4Ti$ with an average value of −263 ± 3 kcal/mole. This disparity probably originates from the estimates of the heats of vaporization and heats of depolymerization of the liquids, rather than the measured heats of formation of the liquids.

3. *Mercury*

The uncertainties in the predicted $\Delta H_f{}^\circ{}_{298}$ are listed as follows: R_2Hg, ±2.7 kcal/mole; RHgX, ±0.9 kcal/mole.

E. MISCELLANEOUS COMPOUNDS

Table XXXI[297–305] includes data for compounds containing unique groups.

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Table XXIX

Organometallic Compounds

Metal	*Compound*	$\Delta H_f{}^\circ{}_{298}$		Δ	*Ref*
		Obsd	*Estd*		
Tin	$(CH_3)_4Sn$	−4.1	−4.1	[0]	292
		−4.6		−0.5	281
	$(CH_3)_3Sn(CH_2CH_3)$	−6.5[a]	−6.3	−0.2	
		−7.1		−0.8	292
	$(CH_3)_3Sn(CH(CH_3)_2)$	−11.2	−10.8	−0.4	290
	$(CH_3)_3Sn(C)CH_3)_3)$	−16.1	−16.1	[0]	290
	$(CH_3)_3SnCH_2C_6H_5$	20.2	20.2	[0]	292
		20.8[a]		−1.1	
	$(CH_3)_3SnC_6H_5$	26.7[a]	26.7	[0]	
		26.1		−1.7	292
	$(CH_3)_3SnCl$	−41.8	−40.0	−1.8	289
	$(CH_3)_2SnCl_2$	−70.6	−69.4	−1.2	289
	CH_3SnCl_3	−99.8	−99.6	−0.2	289
	$(CH_3)_2SnBr$	−32.2	−32.0	−0.2	289
		−33.3		−1.3	
		−33.6		−1.6	
	$(CH_3)_3SnI$	−20.3	−20.3	[0]	289
		−17.8		+2.5	
	$(CH_3)_3(CH_2{=}CH)Sn$	22.1	22.4	−1.4	292
		22.4[a]		[0]	
	$(CH_3)_3SnSn(CH_3)_3$	−7.6	−7.7	+0.1	281
		−5.6		+2.1	292
	$(CH_3CH_2)_4Sn$	−10.7	−12.8	+2.1	281
		−8.1		+4.7	292
	$(CH_3CH_2)_3SnCl$	−46.2	−46.6	+0.4	281, 289
	$(CH_3CH_2)SnCl_3$	−102.0	−101.8	−0.2	281, 289
	$(CH_3CH_2)_3SnSn(CH_2CH_3)_3$	−37.0	−20.8	−16.2	281, 289
	$(CH_3CH_2CH_2)_4Sn$	−34.6	−36.6	+2.0	281, 289
		−33.2		+3.4	
	$(CH_3CH_2CH_2)_3SnH$	−18.8	−16.8	−2.0	291
	$(CH_3)_2CH)_4Sn$	−29.3	−27.9	−1.4	290
	$(CH_3CH_2CH_2CH_2)_4Sn$	−52.9	−52.4	−0.5	281
		−55.9[a]		−3.5	292
	$(CH_3CH_2CH_2CH_2)_3SnH$	−32.2	−31.7	−0.5	291
	$(CH_3CH_2CH_2CH_2)_3SnBr$	−66.0[a]	−68.4	+2.4	292
		−65.5		+2.9	281
	$(CH_3CH_2CH_2CH_2)_3SnCl$		−76.28		
	$(CH_3CH_2CH_2CH_2)SnCl_3$	−113.5[b]	−111.7	−1.8	289
	$(C_6H_5)_4Sn$	114.3	114.3	[0]	294
	$(CH_2{=}CH)_4Sn$		96.32		289
	$(CH_2{=}CH)_3SnCl$	36.8[b]	36.9	[0]	289
	$(CH_2{=}CH)_2SnCl_2$	−20.6[b]	−20.6	[0]	289
	$(CH_2{=}CH)SnCl_3$	−67.1[b]	−67.1	[0]	289
Lead	$(CH_3)_4Pb$	32.6	32.6	[0]	281
	$(CH_3CH_2)_4Pb$	25.8	25.8	[0]	281
Chromium	$((CH_3)_3CO)_4Cr$	−305	−305	[0]	293
Zinc	$(CH_3)_2Zn$	13.1	13.1	[0]	281
	$(CH_3CH_2)_2Zn$	13.0	9.6	+3.4	281
		10.2		+0.6	281
	$(CH_3CH_2CH_2)_2Zn$	−2.2[a]	−0.3	−1.9	281
	$(CH_3CH_2CH_2CH_2)_2Zn$	−12.2[a]	−10.2	−2.0	281, 289
Titanium	$(CH_3CH_2O)_4Ti$	−325	−325	0	293
	$(CH_3CH_2CH_2O)_4Ti$	−354	−345	−9	293
	$((CH_3)_2CHO)_4Ti$	−360	−360	0	293
	$(CH_3CH_2CH_2CH_2O)_4Ti$	−377	−365	−12	293
	$((CH_3)_2CHCH_2O)_4Ti$	−381	−373	−9	293
	$((CH_3)(CH_3CH_2)CHO)_4Ti$	−382	−379	−2	293
	$((CH_3)_3CO)_4Ti$	−395	−398	+3	293
	$(CH_3CH_2CH_2CH_2CH_2O)_4Ti$	−403	−385	−18	293
	$((CH_3)_3CCH_2O)_4Ti$	−438	−418	−20	293
	$((CH_3CH_2)_2N)_4Ti$	−100	−100	[0]	293
Vanadium	$((CH_3)_3CO)_4V$	—328	−328	[0]	293
Cadmium	$(CH_3)_2Cd$	26.2	26.2	[0]	281
	$(CH_3CH_2)_2Cd$	25.5	25.5	[0]	281

Table XXIX (Continued)

Metal	Compound	$\Delta H_f{}^\circ{}_{298}$ Obsd	$\Delta H_f{}^\circ{}_{298}$ Estd	Δ	Ref
Aluminum	$(CH_3)_3Al$	−21.0	−21.0	[0]	281
	$(CH_3CH_2)_3Al$	−19	−19	[0]	281
Germanium	$(CH_3CH_2)_4Ge$	−34.6	−34.9	+0.3	281
	$(CH_3CH_2CH_2)_4Ge$	−54.9	−54.7	−0.2	281
Mercury	$(CH_3)_2Hg$	22.9	22.3	+0.6	295
		22.3		[0]	281
	CH_3HgCl	−12.6	−12.9	+0.3	295
		−12.3		+0.6	281
	CH_3HgBr	−4.7	−5.2	+0.5	295
		−4.4		+0.8	281
	CH_3HgI	5.2	5.7	−0.5	295
		5.3		−0.4	281
	$(CH_3CH_2)_2Hg$	21.9	17.0	+4.9	295
		17.2		+0.2	281
	$(CH_3CH_2)HgCl$	−14.2	−15.6	+1.4	294
		−15.8		−0.2	281
	$(CH_3CH_2)HgBr$	−6.1	−7.88	+1.8	295
		−7.7		+0.2	281
	$(CH_3CH_2)HgI$	4.7	3.0	+1.7	295
		3.1		+0.1	281
	$(CH_3CH_2CH_2)_2Hg$	12.4[a]	7.08	+5.3	296
		6.7		−0.4	281
	$(CH_3CH_2CH_2)HgCl$	−18.6	20.5	+1.9	296
		−20.6		−0.1	281
	$(CH_3CH_2CH_2)HgBr$	−10.6	−12.8	+2.2	296
		−12.7		+0.1	281
	$(CH_3CH_2CH_2)HgI$	0.8	−1.93	+2.7	296
		−1.2		−0.7	281
	$((CH_3)_2CH)_2Hg$	10.4	9.42	+1.0	296
		9.4		[0]	281
	$((CH_3)_2CH)HgCl$	−20.1	−19.4	−0.7	296
		−19.7		−0.3	281
	$((CH_3)_2CH)HgBr$	−13.0	−11.7	−1.3	296
		−12.6		−0.9	281
	$((CH_3)_2CH)HgI$	−1.4	−0.76	−0.6	296
		−1.1		−0.3	281
	$(C_6H_5)_2Hg$	93.8	93.8	[0]	281
		90.9		−2.9	295
		90.5		−3.3	295
	$(C_6H_5)HgCl$	24.6	24.6	[0]	281
		27.4		+2.8	295
	$(C_6H_5)HgBr$	32.6	32.8	−0.2	295
		32.8		[0]	281
	$(C_6H_5)HgI$	42.9	42.6	+0.3	295
		42.6		[0]	281

[a] Heat of vaporization corrected to 25°. [b] See text

Table XXX

Gaseous Heats of Formation of Titanium Alkyloxides

Compound	$\Delta H_f{}^\circ$, kcal/mole for $[Ti\text{-}(O)_4] + 4[O\text{-}(Ti)(C)]$
$[CH_3CH_2O]_4Ti$	−251
$[CH_3(CH_2)_2O]_4Ti$	−260
$[CH_3(CH_2)_3O]_4Ti$	−263
$[CH_3(CH_2)_4O]_4Ti$	−269
$[(CH_3)_2CHO]_4Ti$	−251
$[(CH_3)_2CHCH_2O]_4Ti$	−259
$[(CH_3)(CH_3CH_2)CHO]_4Ti$	−254
$[(CH_3)_3CO]_4Ti$	−248
$[(CH_3CH_2)(CH_3)_2CO]_4Ti$	−285

This section prepared by S. W. Benson and G. R. Haugen.

VIII. Guide to the Use of the Group Tables (Tables XXXIII–XXXVIII)

(a) All values of $\Delta H_f{}^\circ$ are in kcal/mole; S° and $C_p{}^\circ$ are in cal/(deg mole).

(b) Values of properties calculated from the tables may be corrected to any temperature by the approximations[2] (parameters in these equations refer to formation reactions).

$$\Delta H_{T_2}{}^\circ = \Delta H_{T_1}{}^\circ + \overline{\Delta C_p{}^\circ}\,(T_2 - T_1)$$

$$\Delta S_{T_2}{}^\circ = \Delta S_{T_1}{}^\circ + \overline{\Delta C_p{}^\circ}\ln(T_2/T_1)$$

where

$$\overline{\Delta C_p{}^\circ} = 0.5(\Delta C_p{}^\circ{}_{T2} + \Delta C_p{}^\circ{}_{T1})$$

Table XXXI

Compounds Containing Unique Groups

Compound	$\Delta H_f{}^\circ{}_{298}$	$S^\circ{}_{298}$	$C_p{}^\circ$						*Ref*
			300°	*400°*	*500°*	*600°*	*800°*	*1000°*	
SOF		62.87	9.97	10.92	11.63	12.14	12.79	13.15	297
$SOCl_2$	−50.37	73.62	15.94	17.07	17.79	18.28	18.88	19.20	297
SOCl		66.17	10.88	11.62	12.15	12.54	13.03	13.31	297
S_2F_2	−54.5	69.30	15.33	16.83	17.74	18.31	18.94	19.26	297
SF_2	−51.8	60.92	10.44	11.50	12.18	12.63	13.14	13.40	297
SF		54.33	7.57	7.96	8.24	8.44	8.68	8.81	297
S_2Cl_2	−4.75	76.49	17.44	18.37	18.87	19.16	19.46	19.61	297
SCl_2	−5.15	67.20	12.19	12.83	13.18	13.39	13.61	13.71	297
SCl	32.0	57.25	8.20	8.51	8.69	8.81	8.95	9.04	297
$CSCl_2$		70.84	15.34	16.61	17.51	18.10	18.78	19.14	298, 299
H_2S_2	3.9								264
NSF_3		69.37	17.23	19.60	21.17	22.25	23.56	24.29	301
HNCS	30.0	59.15							300
P_2H_4	5.0								280
PBr_3	−28.9								280
PBr_5	−53.0								280
BO_2	(−75)	55.03	10.08	11.17	12.01	12.64	13.45	13.91	297
H_2BOH	−70.0								302
$HB(OH)_2$	−153.8								302
H_3SiBr		62.76	12.69	14.87			20.02		263
H_3SiI		64.54	12.86						263
H_2SiBr_2		73.92	15.68	17.71			21.73		263
$SiBr_4$	−98.0	90.22	23.21	24.23		25.07	25.39	25.54	263
$ClSiBr_3$		90.14	22.78	23.95		24.91	25.31	25.49	263
Cl_2SiBr_2		89.48	22.39	23.69		24.79	25.23	25.47	263
Cl_3SiBr		83.52	21.72	23.35		24.57	25.13	25.35	263
$ISiBr_3$		96.58	23.39	24.35	24.84	25.13	25.42	25.57	263
$Si(CH_3)_4$	(−26)	85.79	33.52	40.32	46.48	51.84	60.55	67.31	263
$(CH_3)_3SiCl$		85.56	31.36	36.94	41.63	45.71	52.15	57.08	304
$(CH_3)_2SiCl_2$	−106.0	86.02	26.17	36.81	34.61	37.72	42.54	46.13	263
$(CH_3)_3SiF$		83.81	29.42	35.09	40.14	44.40	51.30	56.58	303
$(CH_3)_2SiF_2$		80.21	25.26	30.01	33.97	37.17	42.16	45.87	303
CH_3SiF_3		75.07	22.73	26.15		30.54			263
$[(CH_3)_3Si]_2O$		127.85	57.22	68.40	78.16	86.48	99.95	110.33	263
SiI_4	−28.0								263
$(CH_3)_3SiH$	(−21)	79.03	28.36	34.03	39.18	43.46	50.50	55.87	263, 303
$(CH_3)_2SiH_2$	(−17)	71.70	22.03	26.71	30.70	34.24	39.79	43.99	263, 294
CH_3SiH_3	(−12)								
$C_2H_5SiH_3$	(−17)								
$(C_2H_5)_2SiH_2$	(−27)								
$(C_2H_5)_3SiH$	(−36.0)								263
$(C_2H_5)_4Si$	−44.0								263
$C_2H_3SiH_3$	−1.0								263
i-$C_4H_9SiH_3$	−31.0								263
n-$C_4H_9SiH_3$	(−27.0)								263
$(CH_3)_2Si(i-C_3H_7)_2$	−47.0								263
$(C_6H_5)_2SiCl_2$	−50.0								263
$Si(OCH_3)_4$	−300.3								263
$Si(OC_2H_5)_4$	−322.0								263
$Si(O$-$iC_3H_7)_4$	−346.0								263
$Si_2O(OCH_3)_6$	−540.0								263
$Si_3O_2(OCH_3)_8$	−803.0								263
$(CH_3)_2Si(OC_2H_5)_2$	−199.0								263
$(n-C_3H_7)_2Si(OC_2H_5)_2$	−215.0								263
$(CH_3)_2(SiOH)_2O$	−330.0								263
$(CH_3)_2Si(OH)_2$	−192.0								263
$(C_2H_5)_2Si(OH)_2$	−208.0								263
$(C_6H_5)_2Si(OH)_2$	−136.0								263
$Si_2O(CH_3)_6$	−203.0								263
$Si_3O_2(CH_3)_8$	−350.0								263
$Si_3O_2(CH_3)_8$	−351.0								263
$Si_4O_3(CH_3)_{10}$	−405.0								263
	−527.0								263
	−488.0								263

Table XXXI (Continued)

Compound	$\Delta H_f{}^\circ{}_{298}$	$S_{298}{}^\circ$	$C_p{}^\circ$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*Ref*
$Si_5O_4(CH_3)_{12}$	−667.0								263
$Si_2(OCH_3)_8$	−448.0								263
$HC{\equiv}CSiH_3$		64.27	17.31	20.56	23.05	25.05	28.14	30.35	306
H_3SiGeH_3	27.8								305

Table XXXII

Corrections

Group type	*gauche*	*cis*	*ortho*	*Ring or steric strain*	*Other*
Alkanes	$\Delta H_f{}^\circ$	...	...	...	...
Alkenes	$\Delta H_f{}^\circ$	$\Delta H_f{}^\circ$, S°, $C_p{}^\circ$	...	...	...
Alkynes	...	...	...	...	...
Aromatics	...	...	$\Delta H_f{}^\circ$, S°, $C_p{}^\circ$	...	...
Polyaromatics	...	...	$\Delta H_f{}^\circ$, S°, $C_p{}^\circ$	$\Delta H_f{}^\circ$, S°, $C_p{}^\circ$	Conjugation corrections to enthalpy
Ether oxygen	$\Delta H_f{}^\circ$	...	...	...	...
Ditertiary ethers	...	...	...	$\Delta H_f{}^\circ$	...
Aliphatic nitrogen	$\Delta H_f{}^\circ$	...	...	...	...
Pyridine	...	...	$\Delta H_f{}^{\circ a}$	...	...
Halogen (except F)	$\Delta H_f{}^{\circ b}$	...	$\Delta H_f{}^\circ$	...	...
Fluorine	...	...	$\Delta H_f{}^\circ$	...	...
Carbon–boron	$\Delta H_f{}^\circ$	...	...	...	...

[a] Also for *para* substituents. [b] Only for halogen against halogen.

(c) σ is the symmetry number and includes internal, as well as external, symmetry. In these calculations, care must be taken to avoid duplication of rotations as can occur when external and internal rotors share a common axis, *e.g.*, in CH_3–CH_3 for which $\sigma_{int} = 3$ and $\sigma_{ext} = 3 \times 2$, *i.e.*, $\sigma_{tot} = 3 \times 3 \times 2 = 18$. If σ_{int} is calculated as 3×3, then σ_{ext} is only 2; otherwise duplicate rotomers were included in the calculation. For the general molecule, where the above complication is absent, the total symmetry number is evaluated as

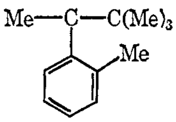
$$\sigma_{tot} = \sigma_{ext} \prod_{i=1}^{i} (\sigma_{int})_i$$

where $(\sigma_{int})_i$ is the rotational degeneracy of the ith rotor, *e.g.*, 3 for methyl, 2 for $-BF_2$, etc., and σ_{ext} is the rotational degeneracy of the molecule as a whole, *e.g.*, 2 for acetone, $CH_3(C{=}O)$-CH_3. The correction $-R \ln \sigma_{tot}$ must be added to a calculated S° value.

(d) If the molecule is optically active, $R \ln n$ must be added to its entropy estimate, where n is the total number of stereomers of equal energy.

(e) Conformational corrections are applied by adding once for each interaction in the molecule, the value of the appropriate correction to the property to be calculated. If no correction is listed, such interaction as may exist is already included in the relevant groups in as many cases as possible.

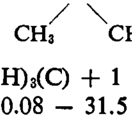
The nature of the estimation of the corrections has already been discussed under the appropriate group type, and their values are listed in the relevant group tables. A summary of the types of correction associated with various classes of compounds is given in Table XXXII. Care should, however, be exercised when calculating properties of any molecule where large groups, several carbon atoms apart, are forced closely together, *e.g.*, in



Predicted values for such compounds may be in error by precisely the value of the distant interaction, *i.e.*, in the above case, the interaction between the *t*-butyl group and the ring hydrogen or methyl. The predicted value thus provides a useful model to estimate the magnitude of such interactions which, as a rough guide, may be expected to arise when atoms can approach to less than the sum of their van der Waals radii. This may be estimated from a molecular model.

(f) Examples

Acetone



$$\begin{aligned} \Delta H_f{}^\circ &= 2 \times C\text{–}(H)_3(C) + 1 \times CO\text{–}(C)_2 \\ &= 2 \times -10.08 - 31.5 = \\ &\qquad -51.66 \text{ kcal/mole } (-51.70 \text{ obsd}) \\ S^\circ &= 2 \times C\text{–}(H)_3(C) + 1 \times CO\text{–}(C)_2 - R \ln \sigma \\ \sigma_{ext} &= 2, \sigma_{int} = 3 \times 3;\ \therefore \sigma_{tot} = 2 \times 3^2 = 18 \\ S^\circ &= 2 \times 30.41 + 15.01 - R \ln 18 = \\ &\qquad 70.1 \text{ cal/mole } (70.5 \text{ obsd}) \end{aligned}$$

---

(306) M. G. Krishna-Pillai, K. Ramaswamy, and S. G. Gnanadesikan, *Czech. J. Phys.*, B16, 150 (1966).

$$
\begin{aligned}
C_p^\circ(300^\circ\mathrm{K}) &= 2 \times \mathrm{C{-}(H)_3(C)} + 1 \times \mathrm{CO{-}(C)_2} \\
&= 2 \times 6.19 + 5.59 = 17.97 \text{ cal/mole}
\end{aligned}
$$

Triethylamine

This has the groups

$$3 \times \mathrm{C{-}(C)(H)_3} + 3 \times \mathrm{C{-}(N)(C)(H)_2} + \mathrm{N{-}(C)_3}$$

$$
\begin{aligned}
\Delta H_f^\circ &= 3 \times -10.08 = -30.24 \\
&+ 3 \times -\ 6.6 \ \ = \underline{-19.8\ \ } \\
&\qquad\qquad\qquad\ -50.04 \\
&+ \qquad 24.4 \ = \qquad +24.4 \\
&+ 3 \text{ gauche interactions} \\
&\qquad \text{at } 0.8 \text{ each } = \underline{+\ 2.4} \\
\therefore \Delta H_f^\circ &= -50.04 + 26.8 = -23.24 \text{ kcal/mole} \\
&\qquad \Delta H_f^\circ \text{ obsd} = -23.9 \ \ \text{kcal/mole}
\end{aligned}
$$

1,1-Dimethylhydrazine

This has the groups

$$\mathrm{C{-}(N)(H)_3} + \mathrm{N{-}(N)(C)_2} + \mathrm{N{-}(N)(H)_2}$$

$\sigma_{\mathrm{rot}} = 3 \times 3 = 9$ and two optical isomers exist

$$
\begin{aligned}
S^\circ &= 2 \times \ \ 30.41 = +60.82 \\
&\ \ \ 1 \times -13.8 \ = \qquad\qquad -13.8 \\
&\ \ \ 1 \times +29.13 = \underline{+29.13} \\
&\qquad\qquad\qquad\ \ +89.95 \\
&-R \ln (3 \times 3/2) = \qquad \underline{-\ 2.98} \\
&\qquad\qquad\qquad\qquad\ \ -16.78
\end{aligned}
$$

i.e.

$S^\circ = +89.95 - 16.78 = 73.17$ cal/mole (obsd 72.82 cal/mole)

This section prepared by S. W. Benson and F. R. Cruickshank.

Together with Dr. S. W. Benson, the authors of the various sections of this joint project were: hydrocarbons, D. M. Golden and H. E. O'Neal; oxygen compounds, R. Shaw; nitrogen compounds, R. Walsh; halogen compounds, A. S. Rodgers; sulfur, boron, and organometallic compounds, G. R. Haugen; sections I, II, VIII, inclusion of recent data, and construction of the whole as a review, F. R. Cruickshank.

Table XXXIII

Hydrocarbon Groups

Group	$\Delta H_f^\circ{}_{298}$	$S^\circ{}_{298}$	C_p°						
			300°	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*
$\mathrm{C{-}(H)_3(C)}$	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
$\mathrm{C{-}(H)_2(C)_2}$	−4.95	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.25
$\mathrm{C{-}(H)(C)_3}$	−1.90	−12.07	4.54	6.00	7.17	8.05	9.31	10.05	11.17
$\mathrm{C{-}(C)_4}$	0.50	−35.10	4.37	6.13	7.36	8.12	8.77	8.76	8.12
$\mathrm{C_d{-}(H)_2}$	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
$\mathrm{C_d{-}(H)(C)}$	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
$\mathrm{C_d{-}(C)_2}$	10.34	−12.7	4.10	4.61	4.99	5.26	5.80	6.08	6.36
$\mathrm{C_d{-}(C_d)(H)}$	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99	9.98
$\mathrm{C_d{-}(C_d)(C)}$	8.88	−14.6	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)	(6.72)
$\mathrm{[C_d{-}(C_B)(H)]}$	6.78	6.4	4.46	5.79	6.75	7.42	8.35	8.99	9.98
$\mathrm{C_d{-}(C_B)(C)}$	8.64	(−14.6)	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)	(6.72)
$\mathrm{[C_d{-}(C_t)(H)]}$	6.78	6.4	4.46	5.79	6.75	7.42	8.35	8.99	9.98
$\mathrm{C{-}(C_d)(C)(H)_2}$	−4.76	9.8	5.12	6.86	8.32	9.49	11.22	12.48	14.36
$\mathrm{C{-}(C_d)_2(H)_2}$	−4.29	(10.2)	(4.7)	(6.8)	(8.4)	(9.6)	(11.3)	(12.6)	(14.4)
$\mathrm{C{-}(C_d)(C_B)(H)_2}$	−4.29	(10.2)	(4.7)	(6.8)	(8.4)	(9.6)	(11.3)	(12.6)	(14.4)
$\mathrm{C{-}(C_t)(C)(H)_2}$	−4.73	10.3	4.95	6.56	7.93	9.08	10.86	12.19	14.20
$\mathrm{C{-}(C_B)(C)(H)_2}$	−4.86	9.3	5.84	7.61	8.98	10.01	11.49	12.54	13.76
$\mathrm{C{-}(C_d)(C)_2(H)}$	−1.48	(−11.7)	(4.16)	(5.91)	(7.34)	(8.19)	(9.46)	(10.19)	(11.28)
$\mathrm{C{-}(C_t)(C)_2(H)}$	−1.72	(−11.2)	(3.99)	(5.61)	(6.85)	(7.78)	(9.10)	(9.90)	(11.12)
$\mathrm{C{-}(C_B)(C)_2(H)}$	−0.98	(−12.2)	(4.88)	(6.66)	(7.90)	(8.75)	(9.73)	(10.25)	(10.68)
$\mathrm{C{-}(C_d)(C)_3}$	1.68	(−34.72)	(3.99)	(6.04)	(7.43)	(8.26)	(8.92)	(8.96)	(8.23)
$\mathrm{C{-}(C_B)(C)_3}$	2.81	(−35.18)	(4.37)	(6.79)	(8.09)	(8.78)	(9.19)	(8.96)	(7.63)
$\mathrm{C_t{-}(H)}$	26.93	24.7	5.27	5.99	6.49	6.87	7.47	7.96	8.85
$\mathrm{C_t{-}(C)}$	27.55	6.35	3.13	3.48	3.81	4.09	4.60	4.92	6.35
$\mathrm{C_t{-}(C_d)}$	29.20	(6.43)	(2.57)	(3.54)	(3.50)	(4.92)	(5.34)	(5.50)	(5.80)
$\mathrm{C_t{-}(C_B)}$	(29.20)	6.43	2.57	3.54	3.50	4.92	5.34	5.50	5.80
$\mathrm{C_B{-}(H)}$	3.30	11.53	3.24	4.44	5.46	6.30	7.54	8.41	9.73
$\mathrm{C_B{-}(C)}$	5.51	−7.69	2.67	3.14	3.68	4.15	4.96	5.44	5.98
$\mathrm{C_B{-}(C_d)}$	5.68	−7.80	3.59	3.97	4.38	4.72	5.28	5.61	5.75
$\mathrm{[C_B{-}(C_t)]}$	5.7	−7.80	3.59	3.97	4.38	4.72	5.28	5.61	5.75
$\mathrm{C_B{-}(C_B)}$	4.96	−8.64	3.33	4.22	4.89	5.27	5.76	5.95	(6.05)
$\mathrm{C_a}$	34.20	6.0	3.9	4.4	4.7	5.0	5.3	5.5	5.7

Table XXXIII (Continued)

Next-Nearest Neighbor Corrections

Group	$\Delta H_f°_{298}$	$S°_{298}$	$C_p°$						
			300°	400°	500°	600°	800°	1000°	1500°
Alkane *gauche* correction	0.80								
Alkene *gauche* correction	0.50								
cis correction	1.00[a]	*b*	−1.34	−1.09	−0.81	−0.61	−0.39	−0.26	0
ortho correction	0.57	−1.61	1.12	1.35	1.30	1.17	0.88	0.66	−0.05

Corrections to be Applied to Ring Compound Estimates

Ring (σ)	$\Delta H_f°_{298}$	$S°_{298}$	$C_p°$						
			300°	400°	500°	600°	800°	1000°	1500°
Cyclopropane (6)	27.6	32.1	−3.05	−2.53	−2.10	−1.90	−1.77	−1.62	(−1.52)
Methylenecyclopropene	40.9								
Cyclopropene (2)	53.7	33.6							
Cyclobutane (8)	26.2	29.8	−4.61	−3.89	−3.14	−2.64	−1.88	−1.38	−0.67
Cyclobutene (2)	29.8	29.0	−2.53	−2.19	−1.89	−1.68	−1.48	−1.33	−1.22
Cyclopentane (10)	6.3	27.3	−7.50	−6.49	−5.40	−4.37	−2.93	−1.93	−0.37
Cyclopentene (2)	5.9	25.8	−5.98	−5.35	−4.89	−4.14	−2.93	−2.26	−1.08
Cyclopentadiene	6.0								
Cyclohexane (6)	0	18.8	−6.40	−4.60	−3.30	−1.60	0.82	1.98	3.19
Cyclohexene (2)	1.4	21.5	−4.28	−3.04	−1.98	−1.43	−0.29	0.08	0.81
Cyclohexadiene-1,3	4.8								
Cyclohexadiene-1,4	0.5								
Cycloheptane (1)	6.4	15.9							
Cycloheptene	5.4								
Cycloheptadiene-1,3	6.6								
Cycloheptatriene-1,3,5 (1)	4.7	23.7							
Cyclooctane (8)	9.9	16.5							
cis-Cyclooctene	6.0								
trans-Cyclooctene	15.3								
Cyclooctatriene-1,3,5	8.9								
Cyclooctatetraene	17.1								
Cyclononane	12.8								
cis-Cyclononene	9.9								
trans-Cyclononene	12.8								
Spiropentane (4)	63.5	67.6							
Bicyclo[1.1.0]butane (2)	67.0	69.2							
Bicyclo[2.1.0]pentane	55.3								
Bicyclo[3.1.0]hexane	32.7								
Bicyclo[4.1.0]heptane	28.9								
Bicyclo[5.1.0]octane	29.6								
Bicyclo[6.1.0]nonane	31.1								

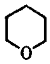
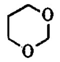
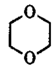
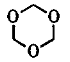
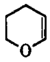
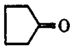
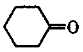
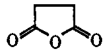
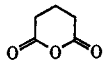
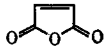
[a] When one of the groups is *t*-butyl, *cis* correction = 4.00; when both are *t*-butyl, *cis* correction = ~10.00; and when there are two *cis* corrections around one double bond, the total correction is 3.00. [b] +1.2 for but-2-ene, 0 for all other 2-enes, and −0.6 for 3-enes.

Table XXXIV

Oxygen-Containing Groups

Group	$\Delta H_f°$	$S°$	$C_p°$						
			300°	400°	500°	600°	800°	1000°	1500°
CO–(CO)(C)	−29.2								
CO–(O)(C_d)	−33.5								
CO–(O)(C_B)	−46.0								
CO–(O)(C)	−33.4	14.78	5.97	6.70		8.02	8.87	9.36	
[CO–(O)(H)[a]]	−29.5	34.93	7.03	7.87	8.82	9.68	11.16	12.20	
CO–(C_d)(H)	−31.7								
CO–$(C_B)_2$	−39.1								
CO–(C_B)(C)	−37.6								
[CO–(C_B)(H)[b]	−31.7								
CO–$(C)_2$	−31.5	15.01	5.59	6.32	7.09	7.76	8.89	9.61	
CO–(C)(H)	−29.6	34.93	7.03	7.87	8.82	9.68	11.16	12.20	
CO–$(H)_2$	−27.7	53.67	8.47	9.38	10.46	11.52	13.37	14.81	
O–$(CO)_2$	−50.9								
O–(CO)(O)	−19.0								
[O–(CO)(C_d)[c]]	−41.3								
O–(CO)(C)	−41.3	8.39							
O–(CO)$(H)_i$	−60.3	24.52	3.81	4.98	5.80	6.34	7.19	7.75	
O–(O)$(O)_i$	(19.0)	(9.4)	(3.7)	(3.7)	(3.7)	(3.7)	(4.2)	(4.2)	(4.8)
O–(O)(C)	(−4.5)	(9.4)	(3.7)	(3.7)	(3.7)	(3.7)	(4.2)	(4.2)	(4.8)
O–(O)(H)	−16.27	27.85	5.17	5.79	6.28	6.66	7.15	7.51	8.17

Table XXXIV (Continued)

Group	$\Delta H_f°$	$S°$	$C_p°$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*
$O{-}(C_d)_2$	−32.8								
$O{-}(C_d)(C)$	−31.3								
$O{-}(C_B)_2$	−19.3								
$O{-}(C_B)(C)$	−22.6								
[$O{-}(C_B)(H)$[d]]	−37.9	29.1	4.3	4.5	4.8	5.2	6.0	6.6	
$O{-}(C)_2$	−23.7	8.68	3.4	3.7	3.7	3.8	4.4	4.6	
$O{-}(C)(H)$	−37.88	29.07	4.33	4.45	4.82	5.23	6.02	6.61	
$C_d{-}(CO)(O)$	6.3								
$C_d{-}(CO)(C)$	9.4								
[$C_d{-}(CO)(H)$[e]]	7.7								
[$C_d{-}(O)(C_d)$[f]]	8.9								
[$C_d{-}(O)(C)$[g]]	10.3								
[$C_d{-}(O)(H)$[h]]	8.6		4.16	5.03	5.81	6.50	7.65	8.45	9.62
$C_B{-}(CO)$	9.7								
$C_B{-}(O)$	−1.8	−10.2	3.9	5.3	6.2	6.6	6.9	6.9	
$C{-}(CO)_2(H)_2$	−7.2								
$C{-}(CO)(C)_3$	1.58								
$C{-}(CO)(C)_2(H)$	−1.83[i]	−12.0							
$C{-}(CO)(C)(H)_2$	−5.0	9.6	6.2	7.7	8.7	9.5	11.1	12.2	
[$C{-}(CO)(H)_3$[j]]	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
$C{-}(O)_2(C)_2$	−16.8								
$C{-}(O)_2(C)(H)$	−17.2								
$C{-}(O)_2(H)_2$	−17.7								
$C{-}(O)(C_B)(H)_2$	−6.6	9.7							
$C{-}(O)(C_d)(H)_2$	−6.9								
$C{-}(O)(C)_3$	−6.60	−33.56	4.33	6.19	7.25	7.70	8.20	8.24	
$C{-}(O)(C)_2(H)$	−7.00	−11.00	4.80	6.64	8.10	8.73	9.81	10.40	
$C{-}(O)(C)(H)_2$	−8.5	10.3	4.99	6.85	8.30	9.43	11.11	12.33	
[$C{-}(O)(H)_3$[k]]	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
Strain									
Ether oxygen *gauche*	0.3								
Ditertiary ethers	8.4								
	27.6	31.4	−2.0	−2.8	−3.0	−2.6	−2.3	−2.3	
	26.4	27.7	−4.6	−5.0	−4.2	−3.5	−2.6	+0.2	
	6.7								
	2.2								
	3.5								
	5.4								
	3.4								
	−6.2								
	2.5								
	6.0								
	3.4								
	1.1								
	1.4								
	4.6								

[a] $CO{-}(O)(H) \equiv CO{-}(C)(H)$, assigned. [b] $CO{-}(C_B)(H) \equiv CO{-}(C_d)(H)$, assigned. [c] $O{-}(CO)(C_d) \equiv O{-}(CO)(C)$, assigned. [d] $O{-}(C_B)(H) \equiv O{-}(C)(H)$, assigned. [e] $C_d{-}(CO)(H) \equiv {}^1/_2[C_d{-}(C_d)(H) + C_d{-}(C)(H)]$, assigned. [f] $C_d{-}(O)(C_d) \equiv C_d{-}(C_d)(C)$, assigned. [g] $C_d{-}(O)(C) \equiv C_d{-}C_2$, assigned. [h] $C_d{-}(O)(H) \equiv C_d{-}(C)(H)$, assigned. [i] Estimated values. [j] $C{-}(CO)(H)_3 \equiv C{-}(C)(H)_3$, assigned. [k] $C{-}(O)(H)_3 \equiv C{-}(C)(H)_3$, assigned.

Table XXXV

Nitrogen-Containing Groups^{a-c}

Group	$\Delta H_f°$	$S°$	$C_p°$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*
$[\mathrm{C{-}(N)(H)_3}]^f$	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
$\mathrm{C{-}(N)(C)(H)_2}$	−6.6	(9.8)^d	(5.25)^d	(6.90)^d	(8.28)^d	(9.39)^d	(11.09)^d	(12.34)^d	
$\mathrm{C{-}(N)(C)_2(H)}$	−5.2	(−11.7)^d	(4.67)^d	(6.32)^d	(7.64)^d	(8.39)^d	(9.56)^d	(10.23)^d	
$\mathrm{C{-}(N)(C)_3}$	−3.2	(−34.1)^d	(4.35)^d	(6.16)^d	(7.31)^d	(7.91)^d	(8.49)^d	(8.50)^d	
$\mathrm{C{-}(N_A)(C)(H)_2}$	(−5.5)	(9.8)							
$\mathrm{C{-}(N_A)(C)_2(H)}$	(−3.3)	(−11.7)							
$\mathrm{C{-}(N_A)(C)_3}$	(−1.9)	(−34.7)							
$\mathrm{N{-}(C)(H)_2}$	4.8	29.71	5.72	6.51	7.32	8.07	9.41	10.47	12.28
$\mathrm{N{-}(C)_2(H)}$	15.4	8.94	4.20	5.21	6.13	6.83	7.90	8.65	9.55
$\mathrm{N{-}(C)_3}$	24.4	−13.46	3.48	4.56	5.43	5.97	6.56	6.67	6.50
$\mathrm{N{-}(N)(H)_2}$	11.4	29.13	6.10	7.38	8.43	9.27	10.54	11.52	13.19
$\mathrm{N{-}(N)(C)(H)}$	20.9	9.61	4.82	5.8	6.5	7.0	7.8	8.3	9.0
$\mathrm{N{-}(N)(C)_2}$	29.2	−13.80							
$\mathrm{N{-}(N)(C_B)(H)}$	22.1								
$\mathrm{N_I{-}(H)}$									
$\mathrm{N_I{-}(C)}$	21.3								
$\mathrm{N_I{-}(C_B)}^e$	16.7								
$\mathrm{N_A{-}(H)}$	25.1	26.8	4.38	4.89	5.44	5.94	6.77	7.42	8.44
$\mathrm{N_A{-}(C)}$	(32.5)	(8.0)							
$\mathrm{N{-}(C_B)(H)_2}$	4.8	29.71	5.72	6.51	7.32	8.07	9.41	10.47	12.28
$\mathrm{N{-}(C_B)(C)(H)}$	14.9								
$\mathrm{N{-}(C_B)(C)_2}$	26.2								
$\mathrm{N{-}(C_B)_2(H)}$	16.3								
$\mathrm{C_B{-}(N)}$	−0.5	−9.69	3.95	5.21	5.94	6.32	6.53	6.56	
$\mathrm{N_A{-}(N)}$	23.0								
$\mathrm{CO{-}(N)(H)}$	−29.6	34.93	7.03	7.87	8.82	9.68	11.16	12.20	
$\mathrm{CO{-}(N)(C)}$	−32.8	16.2	5.37	6.17	7.07	7.66	9.62	11.19	
$\mathrm{N{-}(CO)(H)_2}$	−14.9	24.69	4.07	5.74	7.13	8.29	9.96	11.22	
$\mathrm{N{-}(CO)(C)(H)}$	−4.4	(3.9)^d							
$\mathrm{N{-}(CO)(C)_2}$									
$\mathrm{N{-}(CO)(C_B)(H)}$	+0.4								
$\mathrm{N{-}(CO)_2(H)}$	−18.5								
$\mathrm{N{-}(CO)_2(C)}$	−5.9								
$\mathrm{N{-}(CO)_2(C_B)}$	−0.5								
$\mathrm{C{-}(CN)(C)(H)_2}$	22.5	40.20	11.10	13.40	15.50	17.20	19.7	21.30	
$\mathrm{C{-}(CN)(C)_2(H)}$	25.8	19.80	11.00	12.70	14.10	15.40	17.30	18.60	
$\mathrm{C{-}(CN)(C)_3}$		−2.80							
$\mathrm{C{-}(CN)_2(C)_2}$		28.40							
$\mathrm{C_d{-}(CN)(H)}$	37.4	36.58	9.80	11.70	13.30	14.50	16.30	17.30	
$\mathrm{C_d{-}(CN)_2}$	84.1								
$\mathrm{C_d{-}(NO_2)(H)}$		44.4	12.3	15.1	17.4	19.2	21.6	23.2	25.3
$\mathrm{C_B{-}(CN)}$	35.8	20.50	9.8	11.2	12.3	13.1	14.2	14.9	
$\mathrm{C_t{-}(CN)}$	63.8	35.40	10.30	11.30	12.10	12.70	13.60	14.30	15.30
$\mathrm{C{-}(NO_2)(C)(H)_2}$	−15.1	(48.4)^d							
$\mathrm{C{-}(NO_2)(C)_2(H)}$	−15.8	(26.9)^d							
$\mathrm{C{-}(NO)_2(C)_3}$		(3.9)^d							
$\mathrm{C{-}(NO_2)_2(C)(H)}$	−14.9								
$\mathrm{O{-}(NO)(C)}$	−5.9	41.9	9.10	10.30	11.2	12.0	13.3	13.9	14.5
$\mathrm{O{-}(NO)_2(C)}$	−19.4	48.50							

Corrections to be Applied to Ring Compound Estimates

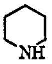
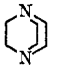
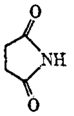
Group	$\Delta H_f°$	$S°$	$C_p°$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*
Ethyleneimine 	27.7	(31.6)^d							
Azetidine 	(26.2)^d	(29.3)^d							
Pyrrolidine 	6.8	26.7	−6.17	−5.58	−4.80	−4.00	−2.87	−2.17	
Piperidine 	1.0								

Table XXXV (Continued)

Group	$\Delta H_f°$	$S°$	$C_p°$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*	*1500°*
	3.4								
	8.5								

[a] N_I = double-bonded nitrogen in imines; $N_I{-}(C_B)$ = pyridine N. N_A = double-bonded nitrogen in azo compounds. [b] No *cis* corrections applied to imines or azo compounds. [c] *gauche* corrections of +0.8 kcal/mole to $\Delta H_f°$ applied just as for hydrocarbons. [d] Estimates by authors; see text under appropriate section. [e] For *ortho* or *para* substitution in pyridine add −1.5 kcal/mole per group. [f] $C{-}(N_A)(H)_3 \equiv C{-}(N)(H)_3 \equiv C{-}(C)(H)_3$ by convention.

Table XXXVI

Approximate Group Contributions to $\Delta H_f°$ at 25° and 1 Atm: Miscellaneous Compounds

Group	$\Delta H_f°$	*Data Sources and References*
$N{-}(NO_2)(C)_2$	17.8	From $\Delta H_f°((CH_3)_2NNO_2) = -0.3$ kcal/mole and $\Delta H_f°((C_2H_5)_2NNO_2) = -13.8$ kcal/mole[a]
$C{-}(N)_3(C)(H)_2$	70	From $\Delta H_f°(C_2H_6N_3) = 59$ kcal/mole (ref 170)
$N{-}(N)(C_B)_2$	36.3	From $\Delta H_f°((C_6H_5)_2NN(C_6H_5)_2) = 144.5$ kcal/mole (ref 119)
$N_I{-}N_I$	21.6	From $\Delta H_f°(C_6H_5CH{=}NN{=}CHC_6H_5) = 104.2$ kcal/mole (ref 138)
$N_I{-}C_B$	14.1	From $\Delta H_f°(C_6H_5CH{=}NC_6H_5) = 61.4$ kcal/mole (ref 138)
$C_B{-}N_I$	−0.5	
$C{-}(NO)(C)(H)_2$	19.1	From $\Delta H_f°(C_2H_5NO) = 9$ kcal/mole, $\Delta H_f°(i\text{-}C_3H_7NO) = 2$ kcal/mole, $\Delta H_f°(t\text{-}C_4H_9NO) = -7$ kcal/mole. These estimates were, in turn, based upon primary, secondary, and tertiary C–NO bond strengths of 38.5, 37, and 35.5 kcal/mole, respectively (see text)
$C{-}(NO)(C)_2(H)$	22.2	
$C{-}(NO)(C)_3$	23.2	
$N{-}(O)(H)_2$	4.8	From $\Delta H_f°(NH_2OH) = -9.3$ kcal/mole $\Delta H_f°(CH_3NHOH) = -12.0$ kcal/mole, and $\Delta H_f°(NH_2OCH_3) = -6.2$ kcal/mole (see text)
$N{-}(O)(C)(H)$	12.2	
$O{-}(N)(H)$	−14.1	
$O{-}(N)(C)$	−0.9	
$N_I{-}(OH){-}5$	—5.0	See text
$C{-}(N)_2(H)_2$	−12.1	From $\Delta H_f°(\mathbf{1}) = 9.4$ kcal/mole (see text)

[a] From R. C. Cass, S. E. Fletcher, C. T. Mortimer, P. G. Quincey, and H. D. Springall, *J. Chem. Soc.*, 958 (1958).

Table XXXVII

Halogen-Containing Groups

Group	$\Delta H_f°$	$S°$	$C_p°$ *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*
$C_d{-}(F)_2$	−77.5	37.3	9.7	11.0	12.0	12.7	13.8	14.5
$C_d{-}(Cl)_2$	−1.8	42.1	11.4	12.5	13.3	13.9	14.6	15.0
$C_d{-}(Br)_2$		47.6	12.3	13.2	13.9	14.3	14.9	15.2
$C_d{-}(F)(Cl)$		39.8	10.3	11.7	12.6	13.3	14.2	14.7
$C_d{-}(F)(Br)$		42.5	10.8	12.0	12.8	13.5	14.3	14.7
$C_d{-}(Cl)(Br)$		45.1	12.1	12.7	13.5	14.1	14.7	
$C_d{-}(F)(H)$	−37.6	32.8	6.8	8.4	9.5	10.5	11.8	12.7
$C_d{-}(Cl)(H)$	2.1	35.4	7.9	9.2	10.3	11.2	12.3	13.1
$C_d{-}(Br)(H)$	12.7	38.3	8.1	9.5	10.6	11.4	12.4	13.2
$C_d{-}(I)(H)$	24.5	40.5	8.8	10.0	10.9	11.6	12.6	13.3
$C_t{-}(Cl)$		33.4	7.9	8.4	8.7	9.0	9.4	9.6
$C_t{-}(Br)$		36.1	8.3	8.7	9.0	9.2	9.5	9.7
$C_t{-}(I)$		37.9	8.4	8.8	9.1	9.3	9.6	9.8
			Arenes					
$C_B{-}(F)$	−42.8	16.1	6.3	7.6	8.5	9.1	9.8	10.2
$C_B{-}(Cl)$	−3.8	18.9	7.4	8.4	9.2	9.7	10.2	10.4
$C_B{-}(Br)$	10.7	21.6	7.8	8.7	9.4	9.9	10.3	10.5
$C_B{-}(I)$	24.0	23.7	8.0	8.9	9.6	9.9	10.3	10.5
$C{-}(C_B)(F)_3$	−162.7	42.8	12.5	15.3	17.2	18.5	20.1	21.0
$C{-}(C_B)(Br)(H)_2$	−6.9							
$C{-}(C_B)(I)(H)_2$	8.4							

Table XXXVII (Continued)

Group	ΔH_f°	S°	C_p° *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*
Corrections for Next-Nearest Neighbors								
ortho (F)(F)	5.0	0	0	0	0	0	0	0
ortho (Cl)(Cl)	2.2							
ortho (alk)(halogen)	0.6							
cis (halogen) (halogen)	(0)							
cis (halogen)(alk)	(0)							
$\mathrm{C{-}(F)_3(C)}$	−158.4	42.5	12.7	15.0	16.4	17.9	19.3	20.0
$\mathrm{C{-}(F)_2(H)(C)}$	(−109.3)	39.1	9.9	12.0		15.1		
$\mathrm{C{-}(F)(H)_2(C)}$	−51.8	35.4	8.1	10.0	12.0	13.0	15.2	16.6
$\mathrm{C{-}(F)_2(C)_2}$	−97.0	17.8	9.9	11.8	13.5			
$\mathrm{C{-}(F)(H)(C)_2}$	−48.4	(14.0)						
$\mathrm{C{-}(F)(C)_3}$	−43.9							
$\mathrm{C{-}(F)_2(Cl)(C)}$	−106.3	40.5	13.7	16.1	17.5			
$\mathrm{C{-}(Cl)_3(C)}$	−20.7	50.4	16.3	18.0	19.1	19.8	20.6	21.0
$\mathrm{C{-}(Cl)_2(H)(C)}$	(−18.9)	43.7	12.1	14.0	15.4	16.5	17.9	18.7
$\mathrm{C{-}(Cl)(H)_2(C)}$	−15.6	37.8	8.9	10.7	12.3	13.4	15.3	16.7
$\mathrm{C{-}(Cl)_2(C)_2}$	(−19.5)							
$\mathrm{C{-}(Cl)(H)(C)_2}$	−12.8	17.6	9.0	9.9	10.5	11.2		
$\mathrm{C{-}(Cl)(C)_3}$	−12.8	−5.4	9.3	10.5	11.0	11.3		
$\mathrm{C{-}(Br)_3(C)}$		55.7	16.7	18.0	18.8	19.4	19.9	20.3
$\mathrm{C{-}(Br)(H)_2(C)}$	−5.4	40.8	9.1	11.0	12.6	13.7	15.5	16.8
$\mathrm{C{-}(Br)(H)(C)_2}$	−3.4							
$\mathrm{C{-}(Br)(C)_3}$	−0.4	−2.0	9.3	11.0				
$\mathrm{C{-}(I)(H)_2(C)}$	7.95	42.5	9.2	11.0	12.9	13.9	15.8	17.2
$\mathrm{C{-}(I)(H)(C)_2}$	10.7	22.2	(8.7)					
$\mathrm{C{-}(I)(C)_3}$	13.0	(0.0)	(9.7)					
$\mathrm{C{-}(Cl)(Br)(H)(C)}$		45.7	12.4	14.0	15.6	16.3	17.9	19.0
$\mathrm{N{-}(F)_2(C)}$	−7.8							
$\mathrm{C{-}(Cl)(C)(O)(H)}$	−22.3	15.4	(9.0)	(9.9)	(10.5)	(11.2)		
Corrections for Next-Nearest Neighbors								
gauche (halogen) (alk)	0.0	0	0	0	0	0	0	0
gauche (halogen) (exclusive of F)	1.0							
gauche (F) (halogen)	0.0							

Table XXXVIII

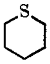
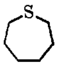
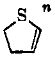
Sulfur-Containing Groups

Group	ΔH_f°	S°	C_p° *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*
$\mathrm{[C{-}(H)_3(S)^{a}]}$	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77
$\mathrm{C{-}(C)(H)_2(S)}$	−5.65	9.88	5.38	7.08	8.60	9.97	12.26	14.15
$\mathrm{C{-}(C)_2(H)(S)}$	−2.64	−11.32	4.85	6.51	7.78	8.69	9.90	10.57
$\mathrm{C{-}(C)_3(S)}$	−0.55	−34.41	4.57	6.27	7.45	8.15	8.72	8.10
$\mathrm{C{-}(C_B)(H)_2(S)}$	−4.73							
$\mathrm{C{-}(C_d)(H)_2(S)}$	−6.45							
$\mathrm{[C_B{-}(S)^{b}]}$	−1.8	10.20	3.90	5.30	6.20	6.60	6.90	6.90
$\mathrm{[C_d{-}(H)(S)^{c}]}$	8.56	8.0	4.16	5.03	5.81	6.50	7.65	8.45
$\mathrm{C_d{-}(C)(S)}$	10.93	−12.41	3.50	3.57	3.83	4.09	4.41	5.00
$\mathrm{S{-}(C)(H)}$	4.62	32.73	5.86	6.20	6.51	6.78	7.30	7.71
$\mathrm{S{-}(C_B)(H)}$	11.96	12.66	5.12	5.26	5.57	6.03	6.99	7.84
$\mathrm{S{-}(C)_2}$	11.51	13.15	4.99	4.96	5.02	5.07	5.41	5.73
$\mathrm{S{-}(C)(C_d)}$	9.97							
$\mathrm{S{-}(C_d)_2}$	−4.54	16.48	4.79	5.58	5.53	6.29	7.94	9.73
$\mathrm{S{-}(C_B)(C)}$	19.16							
$\mathrm{S{-}(C_B)_2}$	25.90							
$\mathrm{S{-}(S)(C)}$	7.05	12.37	5.23	5.42	5.51	5.51	5.38	5.12
$\mathrm{S{-}(S)(C_B)}$	14.5							
$\mathrm{S{-}(S)_2}$	3.04	13.36	4.66	4.97	5.13	5.23	5.33	5.39
$\mathrm{[C{-}(SO)(H)_3{}^{d}]}$	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77
$\mathrm{C{-}(C)(SO)(H)_2}$	−7.72							
$\mathrm{C{-}(C)_3(SO)}$	−3.05							
$\mathrm{C{-}(C_d)(SO)(H)_2}$	−7.35							

Table XXXVIII (*Continued*)

Group	ΔH_f°	S°	C_p° *300°*	*400°*	*500°*	*600°*	*800°*	*1000°*
[C_B–(SO)[e]]	2.3							
SO–$(C)_2$	−14.41	18.10	8.88	10.03	10.50	10.79	10.98	11.17
SO–$(C_B)_2$	−12.0							
[C–$(SO_2)(H)_3$[f]]	−10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77
C–$(C)(SO_2)(H)_2$	−7.68							
C–$(C)_2(SO_2)(H)$	−2.62							
C–$(C)_3(SO_2)$	−0.61							
C–$(C_d)(SO_2)(H)_2$	−7.14							
C–$(C_B)(SO_2)(H)_2$	−5.54							
[C_B–(SO_2)[g]]	2.3							
C_d–$(H)(SO_2)$	12.53							
C_d–$(C)(SO_2)$	14.47							
SO_2–$(C)_2$	−69.74	20.90	11.52					
SO_2–$(C)(C_B)$	−72.29							
SO_2–$(C_B)_2$	−68.58							
[SO_2–$(C_d)(C_B)$[h]]	−68.58							
SO_2–$(C_d)_2$	−73.58							
SO_2–$(SO_2)(C_B)$	−76.25							
[CO–(S)(C)[i]]	−31.56	15.43	5.59	6.32	7.09	7.76	8.89	9.61
S–(H)(CO)	−1.41	31.20	7.63	8.09	8.12	8.17	8.50	8.24
C–$(S)(F)_3$		38.9						
S–(C)(CN)	37.18	41.06	9.51	10.44	11.22	11.86	12.85	13.50
[CS–$(N)_2$[j]]	−31.56	15.43	5.59	6.32	7.09	7.76	8.89	9.61
N–$(CS)(H)_2$	12.78	29.19	6.07	7.28	8.18	8.91	10.09	10.98
[S–(S)(N)[k]]	−4.90							
N–$(S)(C)_2$	29.9							
[SO–$(N)_2$[l]]	−31.56							
N–$(SO)(C)_2$	16.0							
[SO_2–$(N)_2$[m]]	−31.56							
N–$(SO_2)(C)_2$	−20.4							

Organosulfur Compounds Ring Corrections

Ring (σ)										
(a)		(2)	17.7	29.47	−2.85	−2.59	−2.66	−3.02	−4.32	−5.82
(b)		(2)	19.37	27.18	−4.59	−4.18	−3.91	−3.91	−4.60	−5.70
(c)		(2)	1.73	23.56	−4.90	−4.67	−3.68	−3.66	−4.41	−5.57
(d)		(2)	0	17.46	−6.22	−4.26	−2.24	−0.69	0.86	1.29
(e)		(2)	3.89							
(f)		(2)	5.07							
(g)	 [n]	(1)	5.07							
(h)		(2)	5.74							
(i)	 [o]	(2)	1.73	23.56	−4.90	−4.67	−3.68	−3.66	−4.41	−5.57

Organophosphorus Groups[p]

Group	ΔH_f°	S°	*Remarks*
[C–$(P)(H)_3$]	−10.08	30.41	C–$(P)(H)_3$ ≡ C–$(C)(H)_3$, assigned
C–$(P)(C)(H)_2$	−2.47		
[C–$(PO)(H)_3$]	−10.08	30.41	C–$(PO)(H)_3$ ≡ C–$(C)(H)_3$, assigned
C–$(PO)(C)(H)_2$	−3.4		
[C–$(P{:}N)(H)_3$]	−10.08	30.41	C–$(P{:}N)(H)_3$ ≡ C–$(C)(H)_3$, assigned
C–$(N{:}P)(C)(H)_2$	19.4		
[C_B–(P)]	−1.8		C_B–(P) ≡ C_B–(O), assigned
[C_B–(PO)]	2.3		C_B–(PO) ≡ C_B–(CO), assigned
[C_B–(P:N)]	2.3		C_B–(P:N) ≡ C_B–(CO), assigned
P–$(C)_3$	7.04		

Table XXXVIII (Continued)

Group	$\Delta H_f°$	$S°$	*Remarks*
P–(C)(Cl)$_2$	−50.1		
P–(C$_B$)$_3$	28.3		
P–(O)$_3$	−66.8		
[P–(N)$_3$]	−66.8		P–(N)$_3$ ≡ P–(O)$_3$, assigned
PO–(C)$_3$	−72.8		
PO–(C)(F)$_2$		46.77	
PO–(C)(Cl)(F)		50.80	
PO–(C)(Cl)$_2$	−123.0	52.97	
PO–(C)(O)(Cl)	−112.6		
PO–(C)(O)$_2$	−99.5		
PO–(O)$_3$	−104.6		
PO–(O)$_2$(F)	−167.7		
PO–(C$_B$)$_3$	−52.9		
[PO–(N)$_3$]	−104.6		PO–(N)$_3$ ≡ PO–(O)$_3$, assigned
[O–(C)(P)]	−23.5		O–(C)(P) ≡ O–(C)$_2$, assigned
O–(H)(P)	−58.7		
[O–(C)(PO)]	−40.7		O–(C)(PO) ≡ O–(C)(CO), assigned
O–(H)(PO)	−65.0		
O–(PO)$_2$	−54.5		
[O–(P:N)(C)]	−40.7		O–(P:N)(C) ≡ O–(C)(CO), assigned
N–(P)(C)$_2$	32.2		
N–(PO)(C)$_2$	17.8		
[P:N–(C)$_3$(C)]	0.50		P:N–(C)$_3$(C) ≡ C–(C)$_4$, assigned
P:N–(C$_B$)$_3$(C)	−25.7		
P:N–(N:P)(C)$_2$(P:N)	−15.5		
P:N–(N:P)(C$_B$)$_2$(P:N)	−22.9		
P:N–(N:P)(Cl)$_2$(P:N)	−58.2		
P:N–(N:P)(O)$_2$(P:N)	−43.4		

Organoboron Groups[q]

Group	$\Delta H_f°$	*Remarks*
[C–(B)(H)$_3$]	−10.08	C–(B)(H)$_3$ ≡ C–(C)(H)$_3$, assigned
C–(B)(C)(H)$_2$	−2.22	
C–(B)(C)$_2$(H)	1.1	
[C–(BO$_3$)(H)$_3$]	−10.08	C–(BO$_3$)(H)$_3$ ≡ C–(C)(H)$_3$, assigned
C–(BO$_3$)(C)(H)$_2$	−2.2	
C$_d$–(B)(H)	15.6	
B–(C)$_3$	0.9	
B–(C)(F)$_2$	−187.9	
B–(C)$_2$(Cl)	−42.7	
B–(C)$_2$(Br)	−26.9	
B–(C)$_2$(I)	−8.9	
[B–(C)$_2$(O)]	29.3	B–(C)$_2$(O) ≡ N–(C)$_2$(N), assigned
[B–(C$_d$)(F)$_2$]	−192.9	B–(C$_d$)(F)$_2$ ≡ B–(C)(F)$_2$, assigned
[B–(O)$_3$]	24.4	B–(O)$_3$ ≡ B–(N)$_3$, assigned
B–(O)$_2$(Cl)	−19.7	
B–(O)(Cl)$_2$	−61.2	
B–(O)$_2$(H)	19.9	
B–(N)$_3$]	24.4	B–(N)$_3$ ≡ N–(C)$_3$, assigned
B–(N)$_2$(Cl)	−23.8	
B–(N)(Cl)$_2$	−67.9	
BO$_3$–(C)$_3$	−208.7	
O–(B)(H)	−115.5	
O–(B)(C)	−69.43	
N–(B)(C)$_2$	−9.93	
[B–(S)$_3$]	24.4	B–(S)$_3$ ≡ B–(O)$_3$, assigned
S–(B)(C)	−14.5	
S–(B)(C$_B$)	−7.8	

Organometallic Groups[r]

Metal	*Group*	$\Delta H_f°$	*Remarks*
Tin	[C–(Sn)(H)$_3$]	−10.08	C–(Sn)(H)$_3$ ≡ C–(C)(H)$_3$, assigned
	C–(Sn)(C)(H)$_2$	−2.18	
	C–(Sn)(C)$_2$(H)	3.38	
	C–(Sn)(C)$_3$	8.16	
	C–(Sn)(C$_B$)(H)$_2$	−7.77	

Table XXXVIII (Continued)

Metal	*Group*	$\Delta H_f°$	*Remarks*
	[C_B–(Sn)]	5.51	C_B–(Sn) ≡ C_B–(C), assigned
	[C_d–(Sn)(H)]	8.77	C_d–(Sn)(H) ≡ C_d–(C)(H), assigned
	Sn–$(C)_4$	36.2	
	Sn–$(C)_3$(Cl)	−9.8	
	Sn–$(C)_2(Cl)_2$	−49.2	
	Sn–(C)$(Cl)_3$	−89.5	
	Sn–$(C)_3$(Br)	−1.8	
	Sn–$(C)_3$(I)	9.9	
	Sn–$(C)_3$(H)	34.8	
	[Sn–$(C_d)_4$]	36.2	Sn–$(C_d)_4$ ≡ Sn–$(C)_4$, assigned
	Sn–$(C_d)_3$(Cl)	−8.2	
	Sn–$(C_d)_2(Cl)_2$	−50.7	
	Sn–$(C_d)(Cl)_3$	−82.2	
	Sn–$(C)_3(C_d)$	37.6	
	Sn–$(C_B)_4$	26.26	
	Sn–$(C)_3(C_B)$	34.93	
	Sn–$(C)_3$(Sn)	26.4	
Lead	[C–(Pb)$(H)_3$]	−10.08	C–(Pb)$(H)_3$ ≡ C–(C)$(H)_3$, assigned
	C–(Pb)(C)$(H)_2$	−1.70	
	Pb–$(C)_4$	72.9	
Chromium	[O–(Cr)(C)]	−23.5	O–(Cr)(C) ≡ O–(Ti)(C), assigned
	Cr–$(O)_4$	−64.0	
Zinc	[C–(Zn)$(H)_3$]	−10.08	C–(Zn)$(H)_3$ ≡ C–(C)$(H)_3$, assigned
	C–(Zn)(C)$(H)_2$	−1.78	
	Zn–$(C)_2$	33.3	
Titanium	[O–(Ti)(C)]	−23.5	O–(Ti)(C) ≡ O–(P)(C), assigned
	Ti–$(O)_4$	−157	
	[N–(Ti)$(C)_2$]	39.1	N–(Ti)$(C)_2$ ≡ N–(P)$(C)_2$, assigned
	Ti–$(N)_4$	−123	
Vanadium	[O–(V)(C)]	−23.5	O–(V)(C) ≡ O–(Ti)(C), assigned
	V–$(O)_4$	−87.0	
Cadmium	[C–(Cd)$(H)_3$]	−10.08	C–(Cd)$(H)_3$ ≡ C–(C)$(H)_3$, assigned
	C–(C_d)(C)$(H)_2$	−0.30	
	C_d–$(C)_2$	46.4	
Aluminum	[C–(Al)$(H)_3$]	−10.08	C–(Al)$(H)_3$ ≡ C–(C)$(H)_3$, assigned
	C–(Al)(C)$(H)_2$	0.70	
	Al–$(C)_3$	9.2	
Germanium	C–(Ge)(C)$(H)_2$	−7.7	
	[Ge–$(C)_4$]	36.2	Ge–$(C)_4$ ≡ Sn–$(C)_4$, assigned
	Ge–(Ge)$(C)_3$	15.6	
Mercury	[C–(Hg)$(H)_3$]	−10.08	C–(Hg)$(H)_3$ ≡ C–(C)$(H)_3$, assigned
	C–(Hg)(C)$(H)_2$	−2.68	
	C–(Hg)$(C)_2$(H)	3.62	
	[C_B–(Hg)]	−1.8	C_B–(Hg) ≡ C_B–(O), assigned
	Hg–$(C)_2$	42.5	
	Hg–(C)(Cl)	−2.82	
	Hg–(C)(Br)	4.88	
	Hg–(C)(I)	15.78	
	Hg–$(C_B)_2$	64.4	
	Hg–(C_B)(Cl)	9.9	
	Hg–(C_B)(Br)	18.1	
	Hg–(C_B)(I)	27.9	

[a] C–(S)$(H)_3$ ≡ C–(C)$(H)_3$, assigned. [b] C_B–(S) ≡ C_B–(O), assigned. [c] C_d–(S)(H) ≡ C_d–(O)(H), assigned. [d] C–(SO)$(H)_3$ ≡ C–(CO)$(H)_3$, assigned. [e] C_B–(SO) ≡ C_B–(CO), assigned. [f] C–$(SO)_2(H)_3$ ≡ C–(SO)$(H)_3$, assigned. [g] C_B–(SO_2) ≡ C_B–(CO), assigned. [h] SO_2–$(C_d)(C_B)$ ≡ SO_2–$(C_B)_2$, assigned. [i] CO–(S)(C) ≡ CO–$(C)_2$, assigned. [j] CS–$(N)_2$ ≡ CO–$(C)_2$, assigned. [k] S–(S)(N) ≡ O–(O)(C), assigned. [l] SO–$(N)_2$ ≡ CO–$(C)_2$, assigned. [m] SO_2–$(N)_2$ ≡ SO–$(N)_2$, assigned. [n] Assume ring corrections for g and f are the same. [o] Assume ring corrections for i and c are the same. [p] No *gauche* corrections across the X–P, X–PO, and X–P:N bonds (X represents C, O, N). [q] *gauche* corrections across the C–B bond are +0.8 kcal/mole. [r] No *gauche* corrections across C–M bond.