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Group additivity thermodynamic parameters (terms) for Br, Cl, F, CH_3 and OH interactions and CH_3 buttress effects in multi-substituted aromatics

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Abstract

Non-next-nearest neighbor interaction groups which can be used with the Benson group-additivity method for calculation of thermodynamic properties of multi-substituted aromatics have been developed. We report new groups representing ortho, meta and para interactions for $\Delta_f H^\ominus$, $S^\ominus$ and $C_p(T)$ from Br, Cl, F, CH_3 and OH substituents on aromatic rings. The data set will now allow calculation of ΔG and equilibrium constants for reactions of these species over any desired range of temperature when combined with the harmonic oscillator–heat capacity extrapolation in THERM (THERModynamic Estimation of Radicals and Molecules). These interaction groups are used to improve accuracy in calculation of thermodynamic properties for the above multi-substituent aromatic compounds. A comparison of the group additivity estimation with literature values shows improved agreement.

INTRODUCTION

Multi-substituted aromatic or polyaromatic molecules, such as chlorinated dioxins and chlorinated furans, are often observed in the effluent streams from combustion or incineration processes [1]. These compounds are thought to be hazardous and/or toxic and as a consequence are highly undesirable products of incomplete combustion. It would be of significant value to have a knowledge of their fundamental thermodynamic equilibria properties and to have an accurate and fundamental understanding of the reaction pathways of their formation.

In this paper we develop groups which can be used with Benson's group additivity scheme for calculation of the thermodynamic properties of bromo-, chloro-, fluoro- and methyl-substituted aromatics, phenols and ethers. Benson's group method [2–5] has been widely used to estimate enthalpies of formation and Gibbs free energies for reactions of many

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organic species including aromatic and radicals. Benson's group values do not, however, fully account for the steric or electrostatic interactions between adjacent bulky groups or atoms, such as methyls or chlorines on aromatics or alkyl chains, when used for the estimation of the thermodynamic properties of these molecules. These interactions are termed non-text-nearest neighbor interactions because they arise from the substituents on two adjacent central atoms. (A central atom is defined by Benson [3] as an atom bonded to 2 or more substituents.)

We note that some non-text-nearest neighbor interactions are included as gauche or cis/trans interactions in the initial group additivity scheme of Benson [3]. Cohen and Benson [5] have, in addition, recently expanded this non-text-neighbor interaction set in developing a modified set of groups. Here, groups are newly identified to incorporate the number of carbons which are attached to each adjacent carbon of the specific central atom. As an example, T(112) could indicate that the group is a tertiary carbon (c/c3/h) with two of the 3 adjacent carbons being attached to only 1 carbon and the third adjacent carbon being attached to 2 carbons. This is a satisfactory arrangement for alkyl hydrocarbons, where significant sets of thermodynamic data are in the literature and have been reviewed. We have, however, tried this avenue of identification and found that when one needs to consider Cl, F, Br, O, CO, N, etc. attached to each adjacent carbon, the number of central atom groups grows exponentially and rapidly reaches the point where there is nearly one or more than one group for each experimental measurement. This not only severely limits the accuracy one can achieve, but also complicates significantly the present, acceptable, accurate group additivity scheme, which is so useful to engineers, chemists, students, etc.

There is one technique; tri-atom additivity [6], in which the number of types of groups is not even as large as in conventional group additivity. The number of these groups needed for a given molecule is, however, dramatically increased. For example, the simple molecule ethane would have 6 h-c-h groups and 6 h-c-c groups, 12 in total, as compared to only 2 for group additivity. The accuracy of tri-atom additivity is remarkably high even for fluorocarbons [7], but the accurate count of groups for larger molecules (6 groups per C atom in a simple alkane) becomes awkward and confusing to non-expert users. Nor does tri-atom additivity account directly for meta and para interactions on aromatic ring systems. Thus, we recommend continued use of group additivity supplemented with easily defined interaction groups, until a more accurate and rapid technique using a personal computer or work station becomes available: perhaps a quantum mechanics calulation.

We believe it is valuable to correct the values (improve the accuracy) obtained by the group additivity method by including these non-next-nearest neighbor interactions between groups or atoms in aromatic systems

and for other complex molecular systems. Owing to the limited thermodynamic data in the literature [8–15], however, one must often proceed by obtaining the corrections using the method described by Shaub [16, 17]. Shaub has calculated contributions of ortho, meta and para interactions to the enthalpy of formation for methyl, Cl, F and OH substituents on aromatic compounds, where experimental data existed. He then applied the interaction terms to estimate enthalpies of formation at 298 K on a series of compounds which extended beyond the initial species.

The intent of this study is to develop interaction groups, to obtain a knowledge of the thermodynamic properties and to calculate the equilibria at representative combustion temperatures. We develop new values and improve the existing values for enthalpy groups representing non-next-nearest neighbor interactions between substituents (Br, Cl, F, CH_3 and OH) on aromatic rings. We also present data on entropies S° at 298 K and heat capacity $C_p(T)$ (to high temperature) interactions which have not been reported previously. The use of interaction groups also allows a fundamentally more correct central atom group to be derived from thermo data on compounds that do not include the target steric or electrostatic interactions. We therefore, report slightly changed values for some central atom (original Benson) groups in instances where the current literature group is derived from averages of data on several molecules, a number of which contained the interactions.

The data set which includes the $S^{\ominus}$ and $C_p(T)$ terms will now allow calculation of ΔG and equilibrium constants for reactions of these species over any desired range of temperature when combined with the harmonic oscillator-heat capacity extrapolation in THERM (THermodynamic Estimation of Radicals and Molecules) ([18, 19]. The enthalpy corrections obtained in this work are somewhat different from those obtained by Shaub [16]; this results from use of additional literature thermodynamic data in the determinations. We utilize these group values to calculate thermodynamic parameters for a number of multi-substituted aromatic compounds: bromobenzenes, chlorobenzenes, fluorobenzenes, methylbenzenes, methylphenols, chlorofluorobenzenes and chlorobiphenyls. We also present comparison of our calculations with literature values.

PROCEDURE

A data set for groups representing non-next-nearest neighbor interactions from substituents on aromatic rings, such as F, Cl, Br, OH and CH_3, is developed. The method includes selecting representative molecules and their literature thermodynamic properties to define the primary group (Benson-type group) value. We then compute these corrections, i.e. take the differences between the molecular thermodynamic values in the literature for one or a series of molecules for species with the specific group

interaction and those obtained by group additivity. The group additivity values are summed by using a computer code called THERM [18, 19]. The formula to compute the value of the non-next-nearest neighbor interactions is

$$X_{(\alpha\text{-}\alpha)\text{int}} = X_{\text{exp}} - X_{\text{Ga}}$$

where X represents the enthalpy, entropy, or heat capacity interaction values, α is the substituent on the aromatic ring, e.g. F, Cl, CH_3, etc., int is the interaction type (ortho, meta, or para), X_{exp} is the corresponding experimental or literature value and X_{Ga} is the group additivity value obtained by summing the constituent groups of the molecule. The type of interaction is defined as ortho, meta or para. A list of these interactions is given in Table 1.

TABLE 1

Group interaction values for the enthalpy of formation $\Delta_f H^{\ominus}(298)$ in kJ mol^{-1}, entropy $S^{\ominus}(298)$ in J mol^{-1}, and heat capacities $C_p(T)$ in J mol^{-1} K^{-1}

Group [a]	$\Delta_f H^{\ominus}$ (298)	$S^{\ominus}$ (298)	C_p (300)	C_p (400)	C_p (500)	C_p (600)	C_p (800)	C_p (1000)	C_p (1500)	Refs.
ORT/F/F [b]	21.46	0.84	−0.67	−2.22	−2.80	−2.76	−2.01	−1.17	1.63	20, 21
MET/F/F	6.19	−0.71	−0.92	−2.47	−3.22	−3.56	−3.89	−4.44	1.63	20, 21
PAR/F/F	8.74	0.25	−0.25	−1.92	−2.85	−3.35	−3.85	−4.23	1.55	20, 21
ORT/Cl/Cl	8.87	−1.30	−0.84	−1.63	−1.97	−2.01	−1.84	−1.59	2.38	20, 21
MET/Cl/Cl	4.69	0.71	−0.50	−1.38	−1.55	−1.88	−1.80	−1.59	2.38	20, 21
PAR/Cl/Cl	1.34	−0.33	−0.42	−1.21	−1.59	−1.59	−1.55	−1.59	2.51	20, 21
ORT/Br/Br	5.86	−2.30	−0.04	1.21	1.59	1.13	−0.25	−0.96	1.30	21
MET/Br/Br	−0.84	2.76	0.13	1.13	1.38	0.88	−0.42	−1.05	1.17	21
PAR/Br/Br	−0.84	1.34	0.46	1.59	1.88	1.34	−0.08	−0.84	1.38	21
ORT/Cl/F	12.47	0.13	−0.38	−2.09	−2.89	−3.39	−3.64	−4.02	1.92	21
MET/Cl/F	4.85	0.75	0.08	−1.51	−2.30	−2.89	−3.35	−3.81	1.97	21
PAR/Cl/F	4.85	1.21	0.17	−1.55	−2.38	−2.97	−3.31	−3.77	2.05	21
ORT/CH_3/CH_3	3.10	−4.39	4.64	4.27	3.47	2.80	1.67	1.21	0.21	20, 21
MET/CH_3/CH_3	1.34	0.54	−1.92	0.08	0.96	1.21	0.84	0.46	−0.71	20, 21
PAR/CH_3/CH_3	2.05	1.05	−1.59	1.26	2.47	2.76	2.22	1.55	−0.08	20, 21
ORT/CH_3/OH	−1.84	−0.38	4.81	5.15	4.85	4.90	4.77	4.90	–	20, 21
MET/CH_3/OH	−1.38	0.63	3.18	4.27	4.39	4.69	4.81	4.98	–	20, 21
PAR/CH_3/OH	1.38	−1.46	0.08	1.92	1.80	1.84	1.21	1.00	–	20, 21
ORT/CH_3/CH_3 [c]	0.75	−4.39	4.64	4.27	3.47	2.80	1.67	1.21	0.21	20, 21
MET/CH_3/CH_3 [c]	−1.00	0.54	−1.92	0.08	0.96	1.21	0.84	0.46	−0.71	20, 21
PAR/CH_3/CH_3 [c]	−0.29	1.05	−1.59	1.26	2.47	2.76	2.22	1.55	−0.08	20, 21
ORT/CH_3/OH [c]	0.04	−0.71	4.18	4.31	4.14	4.18	4.44	4.48	–	20, 21
MET/CH_3/OH [c]	0.17	0.29	2.55	3.43	3.68	3.97	4.48	4.60	–	20, 21
PAR/CH_3/OH [c]	3.26	−2.13	−1.17	0.25	0.38	0.46	0.50	0.21	–	20, 21
ORT/Cl/OH	18.95									22
MET/Cl/OH	−26.19									22
PAR/Cl/OH	−18.66									22
Cl/OH/Cl [d]	57.95									22
Buttress [e]	1.76	−1.05	1.55	−1.17	−1.59	−1.59	−1.05	−0.21	2.26	21
Buttress [c,e]	5.10	−1.05	1.55	−1.17	−1.59	−1.59	−1.05	−0.21	2.26	21

[a] ORT, Ortho; MET, Meta; PAR, Para. [b] ORT/F/F represents two F atoms on the aromatic ring at the ortho position. [c] Group value determined based on hydrocarbons values from ref. 23. [d] Cl/OH/Cl represents Cl–OH–Cl on adjacent carbons of the aromatic ring. [e] Buttress (1, 2, 3) effect [16], CH_3 on three adjacent carbon atoms, $\Delta_f H^{\ominus}(298)$ determined by optimization.

We have slightly changed the Benson nomenclature for convenience purposes in keying in the data within the THERM computer code. For examples, C–(H)$_3$(C) in Benson became C/C/H3 input to THERM. This notation is shorter and does not require the use of shift keys. The substituted species in the interaction terms and connected atoms in the groups are also listed in alphabetical order.

The values in Table 1 are optimized for di-substituted single-ring aromatics (single interaction only). We also modified several group values from Benson's tables to represent more correctly a single group value (not an average of several species where interactions were also occurring). We feel this allows a more optimal fit when multiple interactions occur on the aromatic ring. A comparison of the difference between Benson's groups and our reported values is shown in Table 2.

TABLE 2

Group differences for the enthalpy of formation $\Delta_f H^\ominus(298)$ in kcal mol^{-1}, entropy $S^\ominus(298)$ in cal mol^{-1} K^{-1}, and heat capacities $C_p(T)$ in cal mol^{-1} K^{-1} between BENSON and THERM in this work [a]

Group [b]		BENSON	THERM	Refs. of THERM
CB/O [b]	$\Delta_f H^\ominus(298)$	−0.9	−1.63	4
	$S^\ominus(298)$	−10.2	−10.04	4
	$C_p(300)$	3.9	4.2	4
	$C_p(400)$	5.3	5.7	4
	$C_p(500)$	6.2	6.54	4
	$C_p(600)$	6.6	6.93	4
	$C_p(800)$	6.9	7.07	4
	$C_p(1000)$	6.9	7.09	4
CB/F [c]	$\Delta_f H^\ominus(298)$	−42.8	−44.36	20
	$S^\ominus(298)$	16.1	15.96	20
	$C_p(300)$	6.3	6.32	20
	$C_p(400)$	7.6	7.75	20
	$C_p(500)$	8.5	8.74	20
	$C_p(600)$	9.1	9.43	20
	$C_p(800)$	9.8	10.28	20
	$C_p(1000)$	10.2	10.78	20
CB/Br [d]	$\Delta_f H^\ominus(298)$	8.5	8.60	20
	$C_p(300)$	7.8	7.59	20
	$C_p(400)$	8.7	8.37	20
	$C_p(500)$	9.4	9.00	20
	$C_p(600)$	9.9	9.51	20
	$C_p(800)$	10.3	10.23	20
	$C_p(1000)$	10.5	10.60	20
CB/Cl [e]	$\Delta_f H^\ominus(298)$	−3.8	−4.11	20
	$S^\ominus(298)$	18.9	18.55	20
	$C_p(300)$	7.4	7.17	20
	$C_p(400)$	8.4	8.35	20
	$C_p(500)$	9.2	9.16	20

TABLE 2 (continued)

Group [b]		BENSON	THERM	Refs. of THERM
	$C_p(600)$	9.7	9.71	20
	$C_p(800)$	10.2	10.34	20
	$C_p(1000)$	10.4	10.68	20
ORT/F/F [f]	$\Delta_f H^{\ominus}(298)$	5.0	5.13	20
	$S^{\ominus}(298)$	0	0.20	20
	$C_p(300)$	0	−0.16	20
	$C_p(400)$	0	−0.53	20
	$C_p(500)$	0	−0.67	20
	$C_p(600)$	0	−0.66	20
	$C_p(800)$	0	−0.48	20
	$C_p(1000)$	0	−0.28	20
ORT/Cl/Cl [g]	$\Delta_f H^{\ominus}(298)$	2.2	2.12	21
C/C/H3 [h]	$\Delta_f H^{\ominus}(298)$	−10.20	−10.01	23
C/C3/H [h]	$\Delta_f H^{\ominus}(298)$	−1.90	−2.25	23
CB/C [h]	$\Delta_f H^{\ominus}(298)$	5.51	5.60	23

[a] Units of kcal mol^{-1} and cal mol^{-1} K^{-1} have been retained for comparison with earlier published data (1 cal = 4.184 J). [b] $C_B(O)$ in Benson. [c] C_B–(Br) in Benson. [d] C_B–(Br) in Benson. [e] C_B–(Cl) in Benson. [f] Ortho (F)(F) in Benson. [g] Ortho (Cl)(Cl) in Benson; Benson has $\Delta_f H^{\ominus}(298)$ only. [h] Use only with the interaction groups derived by Cohen's values.

Analysis of the thermodynamic literature indicates that these interaction effects are not always linearly additive. We have, therefore, developed (empirically) a formalism for counting the number of interactions in order to obtain accurate thermodynamic estimations for multiple-substituted aromatics.

Single substituents on the aromtic ring

This formalism counts all the ortho interactions but only considers the integer value from half of the number of meta and/or para interactions if, and only if, there is more than one type of interaction for the same substituent, e.g. only F or only CH_3.

The calculation for aromatics with only one type of interaction includes all the interactions and is represented by

$$X = X_{Ga} + \text{number of interaction(s)}$$

The calculation for aromatics with more than one type of interaction for the same substituent is

$$X = X_{Ga} + \text{all ortho interaction(s)} + \text{integer}[0.5(\text{number of meta} + \text{para interactions})]$$

If there is only one type of interaction, e.g. 1,3,5-trichlorobenzene, which has only meta Cl/Cl interactions, then all the interactions are counted, 3 in this case

$$X_{\text{1,3,5-trichlorobenzene}} = X_{\text{Ga}} + 3X_{\text{(MET/Cl/Cl)}}$$

There is also one case in which interactions between two different groups, specifically Cl and F, yield optimum results when counted in this way. Therefore, the counting scheme for aromatics with Cl substituents only, F substituents only, or Cl plus F substituents only, is the same; that is, the all-ortho interaction plus half the number of meta and para interactions are counted.

Multiple substituents on the aromatic ring

When the interactions are between different substituents, e.g. Cl and OH or CH_3 and OH, the full number of interactions (not the integer value of half of the number of meta and para interactions) is used in the calculation. (This excludes Cl–F substituent interactions, because they are considered equivalent, see above.)

Table 3 summarizes this counting scheme. Several examples are given below.

TABLE 3

Summary of counting rules

One type of interaction	$X = X_{\text{Ga}}$ + number of interaction(s)
Two or more types of interactions from same substituent	$X = X_{\text{Ga}}$ + all ortho interaction(s) + integer [0.5 (number of meta + para interactions)]
Interactions between Cl and F substituent (considered as equivalent species, i.e. treat same as single substituent)	$X = X_{\text{Ga}}$ + all ortho interaction(s) + integer [0.5 (number of meta + para interactions)]
Multiple substituents (exclude Cl/F)	$X = X_{\text{Ga}}$ + all interaction(s) between different substituents + {all ortho interaction(s) + integer [0.5 (number of meta + para interactions)] from same substituent}

Types: ortho, meta and para. Substituents: Br, Cl, F, CH_3, and OH.

Examples

Pentafluorobenzene

The number of F/F interactions for pentafluorobenzene is 4 ortho, 4 meta and 2 para F/F, but the effective number input to the thermodynamic property calculation is 4 ortho, 2 meta and 1 para F/F:

$$X_{\text{pentafluorobenzene}} = X_{\text{Ga}} + 4X_{(\text{ORT/F/F})} + 2X_{(\text{MET/F/F})} + 1X_{(\text{PAR/F/F})}$$

1,2,3,5-Tetrabromobenzene

1,2,3,5-Tetrabromobenzene would have 2 ortho, 3 meta and 1 para, but only 2 ortho and 1 meta are counted:

$$X_{\text{1,2,3,5-tetrabromobenzene}} = X_{\text{Ga}} + 2X_{(\text{ORT/Br/Br})} + 1X_{(\text{met/Br/Br})}$$

1,2-Dichloro-4,5-difluorobenzene

The interactions for 1,2-dichloro-4,5-difluorobenzene are 1 ortho Cl/Cl, 1 ortho F/F, 2 meta and 1 para Cl/F. However, only 1 ortho Cl/Cl, 1 ortho F/F, 1 meta Cl/F and 1 para Cl/F are counted (Cl/F interactions are treated as same substituent):

$$X_{\text{1,2-dichloro-4,5-difluorobenzene}} = X_{\text{Ga}} + 1X_{(\text{ORT/Cl/Cl})} + 1X_{(\text{ORT/F/F})} + 1X_{(\text{MET/Cl/F})} + 1X_{(\text{PAR/Cl/F})}$$

2,3-Xylenol (2,3-methylphenol)

2,3-Xylenol would have 1 ortho interaction between CH_3 groups (ORT/CH3/CH3), 1 ortho and 1 meta interaction between CH_3 and OH (ORT/CH3/OH and MET/CH3/OH) and all of these interactions are counted:

$$X_{\text{2,3-xylenol}} = X_{\text{Ga}} + 1X_{(\text{ORT/CH3/CH3})} + 1X_{(\text{ORT/CH3/OH})} + 1X_{(\text{MET/CH3/OH})}$$

The empirical counting method was derived from comparison with the literature data for multi-substituted benzenes, and the realization that the effects of these interactions in multi-substituted aromatics are not linearly additive. It results from comparison of our calculation results using different schemes with known literature values.

BUTTRESS EFFECT

In the case where there are three or more adjacent bulky groups, such as methyl groups on three adjacent carbon atoms of the aromatic compound, we have to consider additional corrections for the interaction and restricted rotation of the central methyl group(s). This correction which is called the buttress correction or buttress effect [15] has again been calculated from the observed difference between the experimental values and those obtained from group additivity after correction for ortho, meta and para interactions.

Consider 1,2,3,4-tetramethylbenzene; here the effective number of interactions is 3 ortho and 1 meta CH_3/CH_3, plus 2 buttress corrections:

$$X_{\text{1,2,3,4-tetramethylbenzene}} = X_{\text{Ga}} + 3X_{\text{(ORT/CH3/CH3)}} + 1X_{\text{(MET/CH3/CH3)}} + 2X_{\text{buttress}}$$

Tables 4–9 list results for the thermodynamic estimation on a number of molecules from the group additivity calculation method, comparing the interaction terms with estimates obtained using Benson's groups only, in addition to comparison with the literature values. The compound classes are: flurobenzenes, chlorobenzenes, bromobenzenes, methylbenzenes ($\Delta_f H^{\ominus}$ is listed in Table 16a), and chlorobiphenyls. Reference 21 gives values from the Thermodynamics Research Center/Texas A&M University. THERM denotes the calculation results from this work. DEV is the deviation between the literature values and the results from this study. BENSON is the calculation result using Benson's group calculations which only include ortho interactions. DEV-B is the difference between the literature values and the results from Benson's group calculations.

TABLE 4

Enthalpy of formation at 298 K, $\Delta_f H^{\ominus}$ in kJ mol^{-1}

Species	Ref. 21	THERM [a]	DEV [b]	BENSON [c]	DEV-B [d]
Fluorobenzene	−116.32	−116.57	0.25	−110.04	−6.28
1,2-Difluorobenzene	−294.51	−294.51	0.00	−282.00	−12.51
1,3-Difluorobenzene	−309.99	−309.78	−0.21	−302.92	−7.07
1,4-Difluorobenzene	−307.40	−307.23	−0.17	−302.92	−4.48
1,2,3-Trifluorobenzene	−459.82	−472.46	12.64	−453.96	−5.86
1,2,4-Trifluorobenzene	−481.58	−493.92	12.34	−474.88	−6.69
1,3,5-Trifluorobenzene	−503.34	−496.81	−6.53	−495.80	−7.53
1,2,3,4-Tetrafluorobenzene	−633.46	−644.21	10.75	−625.93	−7.53
1,2,3,5-Trifluorobenzene	−655.21	−665.67	10.46	−646.85	−8.37
1,2,4,5-Trifluorobenzene	−648.10	−656.93	8.83	−646.85	−1.26
Pentafluorobenzene	−807.09	−807.22	0.13	−797.89	−9.20
Hexafluorobenzene	−957.30	−957.51	0.21	−948.93	−8.37
Chlorobenzene	51.09	51.84	−0.75	53.14	−2.05
1,2-Dichlorobenzene	29.71	29.71	0.00	32.64	−2.93
1,3-Dichlorobenzene	25.52	25.52	0.00	23.43	2.09
1,4-Dichlorobenzene	22.18	22.18	0.00	23.43	−1.26
1,2,3-Trichlorobenzene	9.00	7.57	1.42	12.13	−3.14
1,2,4-Trichlorobenzene	−0.21	−1.30	1.09	2.93	−3.14
1,3,5-Trichlorobenzene	−6.90	3.89	−10.79	−6.28	−0.63
1,2,3,4-Tetrachlorobenzene	−9.62	−9.87	0.25	−8.37	−1.26
1,2,3,5-Tetrachlorobenzene	−20.08	−18.74	−1.34	−17.57	−2.51
1,2,4,5-Tetrachlorobenzene	−23.43	−17.41	−6.02	−17.57	−5.86
Pentachlorobenzene	−29.08	−25.98	−3.10	−28.87	−0.21
Hexachlorobenzene	−33.89	−34.56	0.67	−40.17	6.28
Bromobenzene	104.18	105.02	−0.84	104.60	−0.42
1,2-Dibromobenzene	130.54	133.05	−2.51	128.74	1.80
1,3-Dibromobenzene	125.52	126.36	−0.84	126.36	−0.84
1,4-Dibromobenzene	125.52	126.36	−0.84	126.36	−0.84
1,2,3-Tribromobenzene	159.41	161.08	−1.67	152.88	6.53

TABLE 4 (continued)

Species	Ref. 21	THERM [a]	DEV [b]	BENSON [c]	DEV-B [d]
1,2,4-Tribromobenzene	151.88	155.23	−3.35	150.50	1.38
1,3,5-Tribromobenzene	146.86	146.86	0.00	148.11	−1.26
1,2,3,4-Tetrabromobenzene	188.28	188.28	0.00	177.03	11.25
1,2,3,5-Tetrabromobenzene	180.75	182.42	−1.67	174.64	6.11
1,2,4,5-Tetrabromobenzene	178.24	181.59	−3.35	174.64	3.60
Pentabromobenzene	217.15	214.64	2.51	201.17	15.98
Hexabromobenzene	256.06	247.69	8.37	227.69	28.37
2-Chloro-1,1′-biphenyl	158.99	153.59	5.40	152.26	6.74
3-Chloro-1,1′-biphenyl	153.59	150.92	2.68	149.87	3.72
4-Chloro-1,1′-biphenyl	152.30	150.25	2.05	149.87	2.43
2,2′-Dichloro-1,1′-biphenyl	127.61	127.61	0.00	124.93	2.68
2,3-Dichloro-1,1′-biphenyl	135.98	133.80	2.18	131.75	4.23
2,3′-Dichloro-1,1′-biphenyl	128.91	124.93	3.97	122.55	6.36
2,4-Dichloro-1,1′-biphenyl	128.91	128.95	−0.04	122.55	6.36
2,4′-Dichloro-1,1′-biphenyl	128.91	124.26	4.64	122.55	6.36
2,5-Dichloro-1,1′-biphenyl	128.91	126.27	2.64	122.55	6.36
2,6-Dichloro-1,1′-biphenyl	128.91	132.30	−3.39	124.93	3.97
3,3-Dichloro-1,1′-biphenyl	122.21	122.26	−0.04	120.16	2.05
3,4-Dichloro-1,1′-biphenyl	129.29	126.61	2.68	122.55	6.74
3,4′-Dichloro-1,1′-biphenyl	122.21	121.59	0.63	120.16	2.05
3,5-Dichloro-1,1′-biphenyl	122.21	126.94	−4.73	120.16	2.05
4,4′-Dichloro-1,1′-biphenyl	120.92	120.92	0.00	120.16	0.75
2,2′,3-Trichloro-1,1′-biphenyl	106.69	107.82	−1.13	104.43	2.26
2,2′,4-Trichloro-1,1′-biphenyl	99.58	102.97	−3.39	95.23	4.35
2,2′,5-Trichloro-1,1′-biphenyl	99.58	100.29	−0.71	95.23	4.35
2,2′,6-Trichloro-1,1′-biphenyl	99.58	106.32	−6.74	97.61	1.97
2,3,3′-Trichloro-1,1′-biphenyl	106.69	105.14	1.55	102.05	4.64
2,3,4-Trichloro-1,1′-biphenyl	116.32	113.34	2.97	111.25	5.06
2,3,4′-Trichloro-1,1′-biphenyl	106.69	104.47	2.22	102.05	4.64
2,3,5-Trichloro-1,1-biphenyl	106.69	105.14	1.55	102.05	4.64
2,3,6-Trichloro-1,1′-biphenyl	106.69	107.82	−1.13	104.43	2.26
2,3′,4-Trichloro-1,1′-biphenyl	99.58	100.29	−0.71	92.84	6.74
2,3′,5-Trichloro-1,1′-biphenyl	99.58	97.61	1.97	92.84	6.74
2,3′,5′-Trichloro-1,1′-biphenyl	99.58	100.96	−1.38	92.84	6.74
2,3′,6-Trichloro-1,1′-biphenyl	99.58	103.64	−4.06	95.23	4.35
2,4,4′-Trichloro-1,1′-biphenyl	99.58	99.62	−0.04	92.84	6.74
2,4,5-Trichloro-1,1′-biphenyl	106.69	104.47	2.22	102.05	4.64
2,4,6-Trichloro-1,1′-biphenyl	99.58	112.34	−12.76	95.23	4.35
2,4′,5-Trichloro-1,1′-biphenyl	99.58	96.94	2.64	92.84	6.74
2,4′,6-Trichloro-1,1′-biphenyl	99.58	102.97	−3.39	95.23	4.35
2′,3,4-Trichloro-1,1′-biphenyl	106.69	104.47	2.22	102.05	4.64
3,3′,4-Trichloro-1,1′-biphenyl	100.00	101.80	−1.80	99.66	0.33
3,3′,5-Trichloro-1,1′-biphenyl	92.88	98.28	−5.40	90.46	2.43
3,4,4′-Trichloro-1,1′-biphenyl	100.00	101.13	−1.13	99.66	0.33
3,4,5-Trichloro-1,1′-biphenyl	109.62	115.35	−5.73	108.87	0.75
3,4′,5-Trichloro-1,1′-biphenyl	92.88	97.61	−4.73	90.46	2.43

[a] Calculation results from this work.
[b] DEV: deviation between the literature values and the results from this study.
[c] BENSON: calculation results using Benson's group calculations which only include ortho interactions.
[d] DEV-B: deviation between the literature values and the results from Benson's group calculations.

TABLE 5

Entropy at 298 K, $S^{\ominus}$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Fluorobenzene	302.67	302.21	0.46	302.80	−0.13
1,2-Difluorobenzene	322.17	321.58	0.59	321.92	0.25
1,3-Difluorobenzene	321.41	320.03	1.38	321.92	−0.50
1,4-Difluorobenzene	315.56	315.26	0.29	316.18	−0.63
1,2,3-Trifluorobenzene	338.15	340.95	−2.80	341.04	−2.89
1,2,4-Trifluorobenzene	345.77	345.89	−0.13	346.81	−1.05
1,3,5-Trifluorobenzene	329.95	325.64	4.31	329.53	0.42
1,2,3,4-Tetrafluorobenzene	358.86	359.61	−0.75	360.16	−1.30
1,2,3,5-Trifluorobenzene	358.49	358.78	−0.29	360.16	−1.67
1,2,4,5-Trifluorobenzene	353.21	353.30	−0.08	354.43	−1.21
Pentafluorobenzene	377.69	378.53	−0.84	379.28	−1.59
Hexafluorobenzene	382.67	383.13	−0.46	383.51	−0.84
Chlorobenzene	314.01	313.05	0.96	314.51	−0.50
1,2-Dichlorobenzene	341.83	341.12	0.71	345.35	−3.51
1,3-Dichlorobenzene	343.55	343.13	0.42	345.35	−1.80
1,4-Dichlorobenzene	336.73	336.35	0.38	339.62	−2.89
1,2,3-Trichlorobenzene	369.57	369.20	0.38	376.18	−6.61
1,2,4-Trichlorobenzene	376.48	376.27	0.21	381.96	−5.48
1,3,5-Trichlorobenzene	362.71	362.42	0.29	364.68	−1.97
1,2,3,4-Tetrachlorobenzene	397.19	397.98	−0.79	407.02	−9.83
1,2,3,5-Tetrachlorobenzene	399.53	399.28	0.25	407.02	−7.49
1,2,4,5-Tetrachlorobenzene	393.51	393.21	0.29	401.29	−7.78
Pentachlorobenzene	425.68	426.43	−0.75	437.86	−12.18
Hexachlorobenzene	436.60	439.03	−2.43	453.80	−17.20
Bromobenzene	326.10	323.97	2.13	325.81	0.29
1,2-Dibromobenzene	361.96	361.96	0.00	361.20	0.75
1,3-Dibromobenzene	367.02	367.02	0.00	367.94	−0.92
1,4-Dibromobenzene	359.87	359.87	0.00	362.21	−2.34
1,2,3-Tribromobenzene	400.99	399.95	1.05	396.60	4.39
1,2,4-Tribromobenzene	410.32	408.02	2.30	409.11	1.21
1,3,5-Tribromobenzene	398.90	401.33	−2.43	398.57	0.33
1,2,3,4-Tetrabromobenzene	438.86	440.70	−1.84	432.00	6.86
1,2,3,5-Tetrabromobenzene	442.42	443.00	−0.59	438.73	3.68
1,2,4,5-Tetrabromobenzene	436.64	438.61	−1.97	433.00	3.64
Pentabromobenzene	476.77	482.79	−6.02	467.39	9.37
Hexabromobenzene	497.23	506.35	−9.12	481.16	16.07
Toluene	321.00	321.37	−0.38	321.37	−0.38
o-Xylene	353.84	354.68	−0.84	352.33	1.51
m-Xylene	358.53	359.61	−1.09	359.07	−0.54
p-Xylene	352.21	354.34	−2.13	353.30	−1.09
1,2,3-Trimethylbenzene	384.64	386.89	−2.26	383.25	1.38
1,2,4-Trimethylbenzene	395.22	398.11	−2.89	395.76	−0.54
1,3,5-Trimethylbenzene	385.60	386.85	−1.26	385.22	0.38
1,2,3,4-Tetramethylbenzene [b]	421.58	419.70	1.88	414.22	7.36
1,2,3,5-Tetramethylbenzene [b]	422.79	425.14	−2.34	420.95	1.84
1,2,4,5-Tetramethylbenzene [b]	416.60	421.45	−4.85	415.18	1.42
Pentamethylbenzene [b]	452.88	453.55	−0.67	445.18	7.70
Hexamethylbenzene [b]	468.61	464.93	3.68	454.47	14.14
2-Chloro-1,1′-biphenyl	423.09	423.17	−0.08	428.44	−5.36
3-Chloro-1,1′-biphenyl	434.72	433.00	1.72	435.18	−0.46
4-Chloro-1,1′-biphenyl	426.52	424.59	1.92	429.45	−2.93

TABLE 5 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
2,2'-Dichloro-1,1'-biphenyl	447.98	447.77	0.21	458.32	−10.33
2,3-Dichloro-1,1'-biphenyl	448.90	450.53	−1.63	459.28	−10.38
2,3'-Dichloro-1,1'-biphenyl	458.19	457.60	0.59	465.05	−6.86
2,4-Dichloro-1,1'-biphenyl	449.61	449.86	−0.25	459.28	−9.67
2,4'-Dichloro-1,1'-biphenyl	449.78	449.15	0.63	459.28	−9.50
2,5-Dichloro-1,1'-biphenyl	450.62	451.50	−0.88	459.28	−8.66
2,6-Dichloro-1,1'-biphenyl	440.20	436.98	3.22	446.81	−6.61
3,3'-Dichloro-1,1'-biphenyl	464.09	467.44	−3.35	471.79	−7.70
3,4-Dichloro-1,1'-biphenyl	460.28	448.44	11.84	459.28	1.00
3,4'-Dichloro-1,1'-biphenyl	461.29	458.98	2.30	466.01	−4.73
3,5-Dichloro-1,1'-biphenyl	456.68	456.64	0.04	460.28	−3.60
4,4'-Dichloro-1,1'-biphenyl	446.68	450.57	−3.89	460.28	−13.60
2,2',3-Trichloro-1,1'-biphenyl	480.20	475.14	5.06	489.15	−8.95
2,2',4-Trichloro-1,1'-biphenyl	480.20	474.47	5.73	489.15	−8.95
2,2',5-Trichloro-1,1'-biphenyl	480.20	476.10	4.10	489.15	−8.95
2,2',6-Trichloro-1,1'-biphenyl	478.19	461.54	16.65	476.64	1.55
2,3,3'-Trichloro-1,1'-biphenyl	481.79	484.97	−3.18	495.89	−14.10
2,3,4-Trichloro-1,1'-biphenyl	476.10	475.22	0.88	495.89	−19.79
2,3,4'-Trichloro-1,1'-biphenyl	476.10	476.52	−0.42	490.11	−14.02
2,3,5-Trichloro-1,1'-biphenyl	476.10	479.19	−3.10	490.11	−14.02
2,3,6-Trichloro-1,1'-biphenyl	473.42	469.36	4.06	483.38	−9.96
2,3',4-Trichloro-1,1'-biphenyl	481.79	484.30	−2.51	495.89	−14.10
2,3',5-Trichloro-1,1'-biphenyl	481.79	485.93	−4.14	495.89	−14.10
2,3',5'-Trichloro-1,1'-biphenyl	476.10	481.20	−5.10	490.11	−14.02
2,3',6-Trichloro-1,1'-biphenyl	472.42	471.37	1.05	483.38	−10.96
2,4,4'-Trichloro-1,1'-biphenyl	476.10	475.85	0.25	490.11	−14.02
2,4,5-Trichloro-1,1'-biphenyl	476.10	476.52	−0.42	490.11	−14.02
2,4,6-Trichloro-1,1'-biphenyl	466.68	464.38	2.30	477.65	−10.96
2,4',5-Trichloro-1,1'-biphenyl	476.10	477.48	−1.38	490.11	−14.02
2,4',6-Trichloro-1,1'-biphenyl	466.68	462.96	3.72	477.65	−10.96
2',3,4-Trichloro-1,1'-biphenyl	481.79	482.29	−0.50	495.89	−14.10
3,3',4-Trichloro-1,1'-biphenyl	490.49	492.12	−1.63	502.62	−12.13
3,3',5-Trichloro-1,1'-biphenyl	484.72	491.03	−6.32	496.85	−12.13
3,4,4'-Trichloro-1,1'-biphenyl	484.72	483.67	1.05	496.85	−12.13
3,4,5-Trichloro-1,1'-biphenyl	478.90	480.03	−1.13	491.12	−12.22
3,4',5-Trichloro-1,1'-biphenyl	478.90	482.62	−3.72	491.12	−12.22

[a] For key, see footnotes to Table 4. [b] Data from ref. 24.

TABLE 6

Heat capacity at 300 K, $C_p(300)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Fluorobenzene	94.89	92.22	0.67	94.14	0.75
1,2-Difluorobenzene	107.32	106.44	0.88	106.94	0.38
1,3-Difluorobenzene	107.11	106.19	0.92	106.94	0.17
1,4-Difluorobenzene	107.07	106.86	0.21	106.94	0.13
1,2,3-Trifluorobenzene	118.99	118.66	0.33	119.75	−0.75
1,2,4-Trifluorobenzene	119.29	119.33	−0.04	119.75	−0.46
1,3,5-Trifluorobenzene	119.16	117.24	1.92	119.75	−0.59
1,2,3,4-Tetrafluorobenzene	131.21	129.96	1.26	132.55	−1.34

TABLE 6 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
1,2,3,5-Tetrafluorobenzene	131.42	130.62	0.79	132.55	−1.13
1,2,4,5-Tetrafluorobenzene	131.71	130.37	1.34	132.55	−0.84
Pentafluorobenzene	143.59	141.00	2.59	145.35	−1.76
Hexafluorobenzene	156.02	151.63	4.39	158.16	−2.13
Chlorobenzene	98.58	97.78	0.79	98.74	−0.17
1,2-Dichlorobenzene	114.01	113.39	0.63	116.15	−2.13
1,3-Dichlorobenzene	114.47	113.72	0.75	116.15	−1.67
1,4-Dichlorobenzene	114.35	113.80	0.54	116.15	−1.80
1,2,3-Trichlorobenzene	129.29	128.99	0.29	133.55	−4.27
1,2,4-Trichlorobenzene	129.70	129.83	−0.13	133.55	−3.85
1,3,5-Trichlorobenzene	129.75	129.16	0.59	133.55	−3.81
1,2,3,4-Tetrachlorobenzene	144.72	144.10	0.63	150.96	−6.23
1,2,3,5-Tetrachlorobenzene	145.27	144.93	0.33	150.96	−5.69
1,2,4,5-Tetrachlorobenzene	145.35	144.52	0.84	150.96	−5.61
Pentachlorobenzene	160.58	158.78	1.80	168.36	−7.78
Hexachlorobenzene	175.77	173.05	2.72	185.77	−10.00
Bromobenzene	100.96	99.54	1.42	100.42	0.54
1,2-Dibromobenzene	117.70	117.70	0.00	124.18	−6.49
1,3-Dibromobenzene	117.86	117.86	0.00	119.50	−1.63
1,4-Dibromobenzene	118.20	118.20	0.00	119.50	−1.30
1,2,3-Tribromobenzene	135.48	135.85	−0.38	147.95	−12.47
1,2,4-Tribromobenzene	135.48	135.90	−0.42	143.26	−7.78
1,3,5-Tribromobenzene	135.31	136.31	−1.00	138.57	−3.26
1,2,3,4-Tetrabromobenzene	153.26	154.14	−0.88	171.71	−18.45
1,2,3,5-Tetrabromobenzene	153.26	154.18	−0.92	167.03	−13.77
1,2,4,5-Tetrabromobenzene	153.26	154.64	−1.38	167.03	−13.77
Pentabromobenzene	171.00	172.88	−1.88	195.48	−24.48
Hexabromobenzene	187.36	191.13	−3.77	223.93	−36.57
Toluene	105.86	104.85	1.00	104.85	1.00
o-Xylene	133.01	133.01	0.00	133.05	−0.04
m-Xylene	126.44	126.44	0.00	128.37	−1.92
p-Xylene	126.78	126.78	0.00	128.37	−1.59
1,2,3-Trimethylbenzene	155.98	162.72	−6.74	161.25	−5.27
1,2,4-Trimethylbenzene	150.54	156.52	−5.98	156.57	−6.02
1,3,5-Trimethylbenzene	148.45	146.11	2.34	151.88	−3.43
1,2,3,4-Tetramethylbenzene [b]	186.98	190.50	−3.51	189.45	−2.47
1,2,3,5-Tetramethylbenzene [b]	181.59	184.31	−2.72	184.77	−3.18
1,2,4,5-Tetramethylbenzene [b]	184.01	181.17	2.85	184.77	−0.75
Pentamethylbenzene [b]	213.38	216.69	−3.31	217.65	−4.27
Hexamethylbenzene [b]	242.59	252.21	−9.62	250.54	−7.95
2-Chloro-1,1′-biphenyl	182.00	181.08	0.92	185.52	−3.51
3-Chloro-1,1′-biphenyl	182.59	181.46	1.13	180.83	1.76
4-Chloro-1,1′-biphenyl	182.59	181.46	1.13	180.83	1.76
2,2′-Dichloro-1,1′-biphenyl	198.70	198.74	−0.04	207.61	−8.91
2,3-Dichloro-1,1′-biphenyl	198.78	198.28	0.50	202.92	−4.14
2,3′-Dichloro-1,1′-biphenyl	198.91	199.12	−0.21	202.92	−4.02
2,4-Dichloro-1,1′-biphenyl	198.78	198.61	0.17	202.92	−4.14
2,4′-Dichloro-1,1′-biphenyl	198.78	199.12	−0.33	202.92	−4.14
2,5-Dichloro-1,1′-biphenyl	198.78	198.70	0.08	202.92	−4.14
2,6-Dichloro-1,1′-biphenyl	198.70	198.24	0.46	207.61	−8.91
3,3′-Dichloro-1,1′-biphenyl	199.49	199.49	0.00	198.24	1.26
3,4-Dichloro-1,1′-biphenyl	199.49	200.71	−1.21	202.92	−3.43
3,4′-Dichloro-1,1′-biphenyl	199.49	199.49	0.00	198.24	1.26

TABLE 6 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
3,5-Dichloro-1,1′-biphenyl	199.49	198.99	0.50	198.24	1.26
4,4′-Dichloro-1,1′-biphenyl	199.49	199.49	0.00	198.24	1.26
2,2′,3-Trichloro-1,1′-biphenyl	214.81	215.94	−1.13	225.02	−10.21
2,2′,4-Trichloro-1,1′-biphenyl	214.81	216.27	−1.46	225.02	−10.21
2,2′,5-Trichloro-1,1′-biphenyl	214.81	216.35	−1.55	225.02	−10.21
2,2′,6-Trichloro-1,1′-biphenyl	214.72	215.89	−1.17	229.70	−14.98
2,3,3′-Trichloro-1,1′-biphenyl	214.10	216.31	−2.22	220.33	−6.23
2,3,4-Trichloro-1,1′-biphenyl	214.10	215.48	−1.38	220.33	−6.23
2,3,4′-Trichloro-1,1′-biphenyl	214.10	216.31	−2.22	220.33	−6.23
2,3,5-Trichloro-1,1′-biphenyl	214.10	216.31	−2.22	220.33	−6.23
2,3,6-Trichloro-1,1′-biphenyl	214.72	215.94	−1.21	225.02	−10.29
2,3′,4-Trichloro-1,1′-biphenyl	214.10	216.65	−2.55	220.33	−6.23
2,3′,5-Trichloro-1,1′-biphenyl	214.10	216.73	−2.64	220.33	−6.23
2,3′,5′-Trichloro-1,1′-biphenyl	214.10	216.65	−2.55	220.33	−6.23
2,3′,6-Trichloro-1,1′-biphenyl	214.72	216.27	−1.55	225.02	−10.29
2,4,4′-Trichloro-1,1′-biphenyl	214.10	216.65	−2.55	220.33	−6.23
2,4,5-Trichloro-1,1′-biphenyl	214.72	216.31	−1.59	220.33	−5.61
2,4,6-Trichloro-1,1′-biphenyl	214.10	215.27	−1.17	225.02	−10.92
2,4′,5-Trichloro-1,1′-biphenyl	214.72	216.73	−2.01	220.33	−5.61
2,4′,6-Trichloro-1,1′-biphenyl	214.10	216.27	−2.18	225.02	−10.92
2′,3,4-Trichloro-1,1′-biphenyl	214.68	216.31	−1.63	220.33	−5.65
3,3′,4-Trichloro-1,1′-biphenyl	214.68	216.69	−2.01	215.64	−0.96
3,3′,5-Trichloro-1,1′-biphenyl	214.68	217.02	−2.34	215.64	−0.96
3,4,4′-Trichloro-1,1′-biphenyl	214.68	216.69	−2.01	215.64	−0.96
3,4,5-Trichloro-1,1′-biphenyl	214.68	215.35	−0.67	215.64	−0.96
3,4′,5-Trichloro-1,1′-biphenyl	214.68	217.02	−2.34	215.64	−0.96

[a] For key, see footnotes to Table 4. [b] Data from ref. 24.

TABLE 7

Heat capacity at 500 K, $C_p(500)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Fluorobenzene	150.62	150.79	−0.17	149.79	0.84
1,2-Difluorobenzene	161.34	161.71	−0.38	162.51	−1.17
1,3-Difluorobenzene	161.38	161.29	0.08	162.51	−1.13
1,4-Difluorobenzene	161.25	161.67	−0.42	162.51	−1.26
1,2,3-Trifluorobenzene	172.38	172.63	−0.25	175.23	−2.85
1,2,4-Trifluorobenzene	172.17	175.44	−3.26	175.23	−3.05
1,3,5-Trifluorobenzene	172.59	168.57	4.02	175.23	−2.64
1,2,3,4-Tetrafluorobenzene	182.42	180.33	2.09	187.95	−5.52
1,2,3,5-Tetrafluorobenzene	182.80	183.13	−0.33	187.95	−5.15
1,2,4,5-Tetrafluorobenzene	183.01	180.29	2.72	187.95	−4.94
Pentafluorobenzene	192.97	185.18	7.78	200.66	−7.70
Hexafluorobenzene	203.38	190.08	13.31	213.38	−10.00
Chlorobenzene	152.55	152.55	0.00	152.72	−0.17
1,2-Dichlorobenzene	166.06	166.06	0.00	168.36	−2.30
1,3-Dichlorobenzene	166.48	166.48	0.00	168.36	−1.88
1,4-Dichlorobenzene	166.44	166.44	0.00	168.36	−1.92
1,2,3-Trichlorobenzene	179.41	179.58	−0.17	184.01	−4.60
1,2,4-Trichlorobenzene	179.66	181.54	−1.88	184.01	−4.35

TABLE 7 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
1,3,5-Trichlorobenzene	179.74	178.87	0.88	184.01	−4.27
1,2,3,4-Tetrachlorobenzene	192.84	191.54	1.30	199.66	−6.82
1,2,3,5-Tetrachlorobenzene	193.18	193.51	−0.33	199.66	−6.49
1,2,4,5-Tetrachlorobenzene	193.26	191.92	1.34	199.66	−6.40
Pentachlorobenzene	206.40	201.92	4.48	215.31	−8.91
Hexachlorobenzene	219.70	211.92	7.78	230.96	−11.25
Bromobenzene	154.77	151.88	2.89	153.55	1.21
1,2-Dibromobenzene	168.28	168.28	0.00	175.48	−7.20
1,3-Dibromobenzene	168.07	168.07	0.00	170.04	−1.97
1,4-Dibromobenzene	168.57	168.57	0.00	170.04	−1.46
1,2,3-Tribromobenzene	183.30	184.68	−1.38	197.40	−14.10
1,2,4-Tribromobenzene	183.30	183.09	0.21	191.96	−8.66
1,3,5-Tribromobenzene	182.84	185.64	−2.80	186.52	−3.68
1,2,3,4-Tetrabromobenzene	198.66	202.46	−3.81	219.33	−20.67
1,2,3,5-Tetrabromobenzene	198.66	200.87	−2.22	213.89	−15.23
1,2,4,5-Tetrabromobenzene	198.66	202.76	−4.10	213.89	−15.23
Pentabromobenzene	214.01	222.13	−8.12	241.25	−27.24
Hexabromobenzene	226.61	241.50	−14.90	268.61	−42.01
Toluene	171.75	168.95	2.80	168.95	2.80
o-Xylene	204.30	204.30	0.00	206.27	−1.97
m-Xylene	201.79	201.79	0.00	200.83	0.96
p-Xylene	203.30	203.30	0.00	200.83	2.47
1,2,3-Trimethylbenzene	241.84	238.07	3.77	243.59	−1.76
1,2,4-Trimethylbenzene	238.03	236.19	1.84	238.15	−0.13
1,3,5-Trimethylbenzene	233.43	235.60	−2.18	232.71	0.71
1,2,3,4-Tetramethylbenzene [b]	276.27	272.80	3.47	280.91	−4.64
1,2,3,5-Tetramethylbenzene [b]	273.01	270.91	2.09	275.47	−2.47
1,2,4,5-Tetramethylbenzene [b]	273.88	274.97	−1.09	275.47	−1.59
Pentamethylbenzene [b]	311.37	309.99	1.38	318.24	−6.86
Hexamethylbenzene [b]	349.28	345.01	4.27	361.00	−11.72
2-Chloro-1,1′-biphenyl	286.39	285.56	0.84	290.45	−4.06
3-Chloro-1,1′-biphenyl	284.80	284.39	0.42	285.01	−0.21
4-Chloro-1,1′-biphenyl	284.68	284.39	0.29	285.01	−0.33
2,2′-Dichloro-1,1′-biphenyl	300.12	301.75	−1.63	311.54	−11.42
2,3-Dichloro-1,1′-biphenyl	300.29	298.61	1.67	306.10	−5.82
2,3′-Dichloro-1,1′-biphenyl	300.29	300.58	−0.29	306.10	−5.82
2,4-Dichloro-1,1′-biphenyl	300.29	299.03	1.26	306.10	−5.82
2,4′-Dichloro-1,1′-biphenyl	300.29	300.58	−0.29	306.10	−5.82
2,5-Dichloro-1,1′-biphenyl	300.29	298.99	1.30	306.10	−5.82
2,6-Dichloro-1,1′-biphenyl	300.12	300.20	−0.08	311.54	−11.42
3,3′-Dichloro-1,1′-biphenyl	298.70	299.41	−0.71	300.66	−1.97
3,4-Dichloro-1,1′-biphenyl	298.70	300.12	−1.42	306.10	−7.41
3,4′-Dichloro-1,1′-biphenyl	298.70	299.41	−0.71	300.66	−1.97
3,5-Dichloro-1,1′-biphenyl	298.70	297.86	0.84	300.66	−1.97
4,4′-Dichloro-1,1′-biphenyl	298.70	299.41	−0.71	300.66	−1.97
2,2′,3-Trichloro-1,1′-biphenyl	314.01	314.80	−0.79	327.19	−13.18
2,2′,4-Trichloro-1,1′-biphenyl	314.01	315.22	−1.21	327.19	−13.18
2,2′,5-Trichloro-1,1′-biphenyl	314.01	315.18	−1.17	327.19	−13.18
2,2′,6-Trichloro-1,1′-biphenyl	313.97	316.39	−2.43	332.63	−18.66
2,3,3′-Trichloro-1,1′-biphenyl	314.13	313.63	0.50	321.75	−7.61
2,3,4-Trichloro-1,1′-biphenyl	314.13	311.67	2.47	321.75	−7.61
2,3,4′-Trichloro-1,1′-biphenyl	314.13	313.63	0.50	321.75	−7.61
2,3,5-Trichloro-1,1′-biphenyl	314.13	313.63	0.50	321.75	−7.61

TABLE 7 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
2,3,6-Trichloro-1,1′-biphenyl	313.97	314.80	−0.84	327.19	−13.22
2,3′,4-Trichloro-1,1′-biphenyl	314.13	314.05	0.08	321.75	−7.61
2,3′,5-Trichloro-1,1′-biphenyl	314.13	314.01	0.13	321.75	−7.61
2,3′,5′-Trichloro-1,-′-biphenyl	314.13	314.05	0.08	321.75	−7.61
2,3′,6-Trichloro-1,1′-biphenyl	313.97	315.22	−1.26	327.19	−13.22
2,4,4′-Trichloro-1,1′-biphenyl	314.13	314.05	0.08	321.75	−7.61
2,4,5-Trichloro-1,1′-biphenyl	314.13	313.63	0.50	321.75	−7.61
2,4,6-Trichloro-1,1′-biphenyl	313.97	312.13	1.84	327.19	−13.22
2,4′,5-Trichloro-1,1′-biphenyl	314.13	314.01	0.13	321.75	−7.61
2,4′,6-Trichloro-1,1′-biphenyl	313.97	315.22	−1.26	327.19	−13.22
2′,3,4-Trichloro-1,1′-biphenyl	314.13	313.63	0.50	321.75	−7.61
3,3′,4-Trichloro-1,1′-biphenyl	311.71	312.46	−0.75	316.31	−4.60
3,3′,5-Trichloro-1,1′-biphenyl	311.71	312.88	−1.17	316.31	−4.60
3,4,4′-Trichloro-1,1′-biphenyl	311.71	312.46	−0.75	316.31	−4.60
3,4,5-Trichloro-1,1′-biphenyl	311.71	308.95	2.76	316.31	−4.60
3,4′,5-Trichloro-1,1′-biphenyl	311.71	312.88	−1.17	316.31	−4.60

[a] For key, see footnotes to Table 4. [b] Data from ref. 24.

TABLE 8

Heat capacity at 800 K, $C_p(800)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Fluorobenzene	199.49	200.75	−1.26	198.74	0.75
1,2-Difluorobenzene	207.65	210.20	−2.55	208.20	−0.54
1,3-Difluorobenzene	207.65	208.32	−0.67	208.20	−0.54
1,4-Difluorobenzene	207.57	208.36	−0.79	208.20	−0.63
1,2,3-Trifluorobenzene	216.44	219.66	−3.22	217.65	−1.21
1,2,4-Trifluorobenzene	216.19	221.67	−5.48	217.65	−1.46
1,3,5-Trifluorobenzene	216.52	212.00	4.52	217.65	−1.13
1,2,3,4-Tetrafluorobenzene	224.26	225.22	−0.96	227.11	−2.85
1,2,3,5-Tetrafluorobenzene	224.56	227.23	−2.68	227.11	−2.55
1,2,4,5-Tetrafluorobenzene	224.60	223.38	1.21	227.11	−2.51
Pentafluorobenzene	232.55	226.94	5.61	236.56	−4.02
Hexafluorobenzene	240.75	230.50	10.25	246.02	−5.27
Chlorobenzene	200.20	201.00	−0.79	200.41	−0.21
1,2-Dichlorobenzene	210.37	210.87	−0.50	211.54	−1.17
1,3-Dichlorobenzene	210.58	210.92	−0.33	211.54	−0.96
1,4-Dichlorobenzene	210.66	211.17	−0.50	211.54	−0.88
1,2,3-Trichlorobenzene	220.45	220.75	−0.29	222.67	−2.22
1,2,4-Trichlorobenzene	220.54	222.59	−2.05	222.67	−2.13
1,3,5-Trichlorobenzene	220.58	219.03	1.55	222.67	−2.09
1,2,3,4-Tetrachlorobenzene	230.58	228.82	1.76	233.80	−3.22
1,2,3,5-Tetrachlroobenzene	230.75	230.66	0.08	233.80	−3.05
1,2,4,5-Tetrachlorobenzene	230.79	229.12	1.67	233.80	−3.01
Pentachlorobenzene	240.75	235.35	5.40	244.93	−4.18
Hexachlorobenzene	250.87	241.58	9.29	256.06	−5.19
Bromobenzene	201.84	200.54	1.30	200.83	1.00
1,2-Dibromobenzene	211.54	211.54	0.00	216.06	−4.52
1,3-Dibromobenzene	211.38	211.38	0.00	212.38	−1.00
1,4-Dibromobenzene	211.71	211.71	0.00	212.38	−0.67

TABLE 8 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
1,2,3-Tribromobenzene	222.59	222.55	0.04	231.29	−8.70
1,2,4-Tribromobenzene	222.59	222.80	−0.21	227.61	−5.02
1,3,5-Tribromobenzene	222.13	221.79	0.33	223.93	−1.80
1,2,3,4-Tetrabromobenzene	234.01	233.13	0.88	246.52	−12.51
1,2,3,5-Tetrabromobenzene	234.01	233.38	0.63	242.84	−8.83
1,2,4,5-Tetrabromobenzene	234.01	233.30	0.71	242.84	−8.83
Pentabromobenzene	245.39	243.63	1.76	261.75	−16.36
Hexabromobenzene	254.43	253.97	0.46	280.66	−26.23
Toluene	234.81	232.97	1.84	232.97	1.84
o-Xylene	278.32	278.32	0.00	280.33	−2.01
m-Xylene	277.48	277.48	0.00	276.65	0.84
p-Xylene	278.86	278.86	0.00	276.65	2.22
1,2,3-Trimethylbenzene	326.56	322.63	3.93	327.69	−1.13
1,2,4-Trimethylbenzene	327.23	322.00	5.23	324.01	3.22
1,3,5-Trimethylbenzene	321.67	322.84	−1.17	320.33	1.34
1,2,3,4-Tetramethylbenzene [b]	371.54	367.77	3.77	375.05	−3.51
1,2,3,5-Tetramethylbenzene [b]	369.78	367.15	2.64	371.37	−1.59
1,2,4,5-Tetramethylbenzene [b]	370.41	370.41	0.00	371.37	−0.96
Pentamethylbenzene [b]	417.48	415.14	2.34	422.42	−4.94
Hexamethylbenzene [b]	465.01	459.86	5.15	473.46	−8.45
2-Chloro-1,1′-biphenyl	378.19	377.02	1.17	378.48	−0.29
3-Chloro-1,1′-biphenyl	374.72	374.51	0.21	374.80	−0.08
4-Chloro-1,1′-biphenyl	374.72	374.51	0.21	374.80	−0.08
2,2′-Dichloro-1,1′-biphenyl	387.98	390.37	−2.38	393.30	−5.31
2,3-Dichloro-1,1′-biphenyl	388.40	386.02	2.38	389.61	−1.21
2,3′-Dichloro-1,1′-biphenyl	388.48	387.86	0.63	389.61	−1.13
2,4-Dichloro-1,1′-biphenyl	388.40	386.06	2.34	389.61	−1.21
2,4′-Dichloro-1,1′-biphenyl	388.40	387.86	0.54	389.61	−1.21
2,5-Dichloro-1,1′-biphenyl	388.48	386.31	2.18	389.61	−1.13
2,6-Dichloro-1,1′-biphenyl	387.98	388.57	−0.59	393.30	−5.31
3,3′-Dichloro-1,1′-biphenyl	384.89	385.35	−0.46	385.93	−1.05
3,4-Dichloro-1,1′-biphenyl	384.89	386.98	−2.09	389.61	−4.73
3,4′-Dichloro-1,1′-biphenyl	384.89	385.35	−0.46	385.93	−1.05
3,5-Dichloro-1,1′-biphenyl	384.89	383.55	1.34	385.93	−1.05
4,4′-Dichloro-1,1′-biphenyl	384.89	385.35	−0.46	385.93	−1.05
2,2′,3-Trichloro-1,1′-biphenyl	398.23	399.36	−1.13	404.43	−6.19
2,2′,4-Trichloro-1,1′-biphenyl	398.23	399.40	−1.17	404.43	−6.19
2,2′,5-Trichloro-1,1′-biphenyl	398.23	399.66	−1.42	404.43	−6.19
2,2′,6-Trichloro-1,1′-biphenyl	398.23	401.92	−3.68	408.11	−9.87
2,3,3′-Trichloro-1,1′-biphenyl	398.74	396.85	1.88	400.74	−2.01
2,3,4-Trichloro-1,1′-biphenyl	398.74	395.01	3.72	400.74	−2.01
2,3,4′-Trichloro-1,1′-biphenyl	398.74	396.85	1.88	400.74	−2.01
2,3,5-Trichloro-1,1′-biphenyl	398.74	396.85	1.88	400.74	−2.01
2,3,6-Trichloro-1,1′-biphenyl	398.23	399.36	−1.13	404.43	−6.19
2,3′,4-Trichloro-1,1′-biphenyl	398.74	396.89	1.84	400.74	−2.01
2,3′,5-Trichloro-1,1′-biphenyl	398.74	397.15	1.59	400.74	−2.01
2,3′,5′-Trichloro-1,1′-biphenyl	398.74	396.89	1.84	400.74	−2.01
2,3′,6-Trichloro-1,1′-biphenyl	398.23	399.40	−1.17	404.43	−6.19
2,4,4′-Trichloro-1,1′-biphenyl	398.74	396.89	1.84	400.74	−2.01
2,4,5-Trichloro-1,1′-biphenyl	398.74	396.85	1.88	400.74	−2.01
2,4,6-Trichloro-1,1′-biphenyl	398.23	395.81	2.43	404.43	−6.19
2,4′,5-Trichloro-1,1′-biphenyl	398.74	397.15	1.59	400.74	−2.01
2,4′,6-Trichloro-1,1′-biphenyl	398.23	399.40	−1.17	404.43	−6.19

TABLE 8 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
2',3,4-Trichloro-1,1'-biphenyl	398.74	396.85	1.88	400.74	−2.01
3,3',4-Trichloro-1,1'-biphenyl	394.59	394.34	0.25	397.06	−2.47
3,3',5-Trichloro-1,1'-biphenyl	394.59	394.38	0.21	397.06	−2.47
3,4,4'-Trichloro-1,1'-biphenyl	394.59	394.34	0.25	397.06	−2.47
3,4,5-Trichloro-1,1'-biphenyl	394.59	390.70	3.89	397.06	−2.47
3,4',5-Trichloro-1,1'-biphenyl	394.59	394.38	0.21	397.06	−2.47

[a] For key, see footnotes to Table 4. [b] Data from ref. 24.

TABLE 9

Heat capacity at 1000 K, $C_p(1000)$ im J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Fluorobenzene	218.91	221.04	−2.13	218.61	0.29
1,2-Difluorobenzene	225.68	229.79	−4.10	226.10	−0.42
1,3-Difluorobenzene	225.68	226.52	−0.84	226.10	−0.42
1,4-Difluorobenzene	225.60	226.73	−1.13	226.10	−0.50
1,2,3-Trifluorobenzene	233.09	238.53	−5.44	233.59	−0.50
1,2,4-Trifluorobenzene	232.80	239.70	−6.90	233.59	−0.79
1,3,5-Trifluorobenzene	233.01	227.57	5.44	233.59	−0.59
1,2,3,4-Tetrafluorobenzene	239.62	242.84	−3.22	241.08	−1.46
1,2,3,5-Tetrafluorobenzene	239.79	244.01	−4.23	241.08	−1.30
1,2,4,5-Tetrafluorobenzene	239.79	239.79	0.00	241.08	−1.30
Pentafluorobenzene	246.60	242.92	3.68	248.57	−1.97
Hexafluorobenzene	253.38	246.06	7.32	256.06	−2.68
Chlorobenzene	219.37	220.62	−1.26	219.45	−0.08
1,2-Dichlorobenzene	227.69	228.53	−0.84	227.78	−0.08
1,3-Dichlorobenzene	227.78	228.53	−0.75	227.78	0.00
1,4-Dichlorobenzene	227.90	228.53	−0.63	227.78	0.13
1,2,3-Trichlorobenzene	235.94	236.44	−0.50	236.10	−0.17
1,2,4-Trichlorobenzene	235.98	238.03	−2.05	236.10	−0.13
1,3,5-Trichlorobenzene	235.98	234.85	1.13	236.10	−0.13
1,2,3,4-Tetrachlorobenzene	244.22	242.76	1.46	244.43	−0.21
1,2,3,5-Tetrachlorobenzene	244.35	244.35	0.00	244.43	−0.08
1,2,4,5-Tetrachlorobenzene	244.35	242.76	1.59	244.43	−0.08
Pentachlorobenzene	252.55	247.48	5.06	252.76	−0.21
Hexachlorobenzene	260.83	252.21	8.62	261.08	−0.25
Bromobenzene	220.71	220.29	0.42	219.87	0.84
1,2-Dibromobenzene	228.49	228.49	0.00	231.38	−2.89
1,3-Dibromobenzene	228.40	228.61	−0.21	228.61	−0.21
1,4-Dibromobenzene	228.61	228.61	0.00	228.61	0.00
1,2,3-Tribromobenzene	237.48	236.69	0.79	242.88	−5.40
1,2,4-Tribromobenzene	237.48	237.65	−0.17	240.12	−2.64
1,3,5-Tribromobenzene	237.11	236.10	1.00	237.36	−0.25
1,2,3,4-Tetrabromobenzene	246.69	244.05	2.64	254.39	−7.70
1,2,3,5-Tetrabromobenzene	246.69	245.02	1.67	251.63	−4.94
1,2,4,5-Tetrabromobenzene	246.69	244.18	2.51	251.63	−4.94
Pentabromobenzene	255.89	250.58	5.31	265.89	−10.00
Hexabromobenzene	263.30	256.98	6.32	280.16	−16.86

TABLE 9 (continued)

Species	Ref. 21	THERM	DEV	BENSON	DEV-B
Toluene	261.54	260.50	1.05	260.50	1.05
o-Xylene	311.08	311.08	0.00	312.63	−1.55
m-Xylene	310.33	310.33	0.00	309.87	0.46
p-Xylene	311.42	311.42	0.00	309.87	1.55
1,2,3-Trimethylbenzene	363.84	361.46	2.38	364.76	−0.92
1,2,4-Trimethylbenzene	365.51	360.45	5.06	362.00	3.51
1,3,5-Trimethylbenzene	360.41	360.62	−0.21	359.24	1.17
1,2,3,4-Tetramethylbenzene [b]	414.38	412.29	2.09	416.89	−2.51
1,2,3,5-Tetramethylbenzene [b]	413.00	411.29	1.72	414.13	−1.13
1,2,4,5-Tetramethylbenzene [b]	413.67	413.04	0.63	414.13	−0.46
Pentamethylbenzene [b]	465.60	464.68	0.92	469.03	−3.43
Hexamethylbenzene [b]	517.90	516.31	1.59	523.92	−6.02
2-Chloro-1,1′-biphenyl	414.89	413.50	1.38	412.75	2.13
3-Chloro-1,1′-biphenyl	410.70	410.49	0.21	409.99	0.71
4-Chloro-1,1′-biphenyl	410.70	410.49	0.21	409.99	0.71
2,2′-Dichloro-1,1′-biphenyl	422.50	425.35	−2.85	423.84	−1.34
2,3-Dichloro-1,1′-biphenyl	423.21	420.74	2.47	421.08	2.13
2,3′-Dichloro-1,1′-biphenyl	423.21	422.33	0.88	421.08	2.13
2,4-Dichloro-1,1′-biphenyl	423.21	420.74	2.47	421.08	2.13
2,4′-Dichloro-1,1′-biphenyl	423.21	422.33	0.88	421.08	2.13
2,5-Dichloro-1,1′-biphenyl	423.21	420.74	2.47	421.08	2.13
2,6-Dichloro-1,1′-biphenyl	422.50	423.76	−1.26	423.84	−1.34
3,3′-Dichloro-1,1′-phenyl	418.99	419.32	−0.33	418.32	0.67
3,4-Dichloro-1,1′-biphenyl	418.99	421.66	−2.68	421.08	−2.09
3,4′-Dichloro-1,1′-biphenyl	418.99	419.32	−0.33	418.32	0.67
3,5-Dichloro-1,1′-biphenyl	418.99	417.73	1.26	418.32	0.67
4,4′-Dichloro-1,1′-biphenyl	418.99	419.32	−0.33	418.32	0.67
2,2′,3-Trichloro-1,1′-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,2′,4-Trichloro-1,1′-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,2′,5-Trichloro-1,1′-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,2′,6-Trichloro-1,1′-biphenyl	430.95	435.60	−4.64	434.93	−3.97
2,3,3′-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3,4-Trichloro-1,1′-biphenyl	431.75	427.98	3.77	429.40	2.34
2,3,4′-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3,5-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3,6-Trichloro-1,1′-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,3′,4-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3′,5-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3′,5′-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,3′,6-Trichloro-1,1′-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,4,4′-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,4,5-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,4,6-Trichloro-1,1′-biphenyl	430.95	429.40	1.55	432.17	−1.21
2,4′,5-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
2,4′,6-Trichloro-1,1-biphenyl	430.95	432.58	−1.63	432.17	−1.21
2,3,4-Trichloro-1,1′-biphenyl	431.75	429.57	2.18	429.40	2.34
3,3′,4-Trichloro-1,1′-biphenyl	426.85	426.56	0.29	426.64	0.21
3,3′,5-Trichloro-1,1′-biphenyl	426.85	426.56	0.29	426.64	0.21
3,4,4′-Trichloro-1,1′-biphenyl	426.85	426.56	0.29	426.64	0.21
3,4,5-Trichloro-1,1′-biphenyl	426.85	423.38	3.47	426.64	0.21
3,4′,5-Trichloro-1,1′-biphenyl	426.85	426.56	0.29	426.64	0.21

[a] For key, see footnotes to Table 4. [b] Data from ref. 24.

Tables 10–15 list the literature thermodynamic properties and predicted results from these calculations and from Benson groups for chlorofluorobenzenes (we note that Benson's groups consider ortho(F)(F) and ortho(Cl)(Cl) interactions only). For this compound series, THERM not only uses the formalism for identical groups, such as Cl/Cl and F/F, but also considers the interactions between Cl and F as identical groups for counting. The counting will then utilize all ortho interactions and the integer value of half of the meta and/or para interactions. DEV is the deviation between the literature values and the calculated results from THERM. As shown in these tables, counting formalisms from THERM generate smaller deviations than the Benson groups, for most of the chlorofluorobenzenes.

TABLE 10

Enthalpy of formation of chlorofluorobenzenes at 298 K, $\Delta_f H^{\ominus}$ in kJ mol^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	−135.10	−135.10	0.00	−137.36	2.26
1-Chloro-3-fluorobenzene	−142.72	−142.72	0.00	−139.75	−2.97
1-Chloro-4-fluorobenzene	−142.72	−142.72	0.00	−139.75	−2.97
1-Chloro-2,3-difluorobenzene	−303.80	−313.05	9.25	−309.32	5.52
1-Chloro-2,4-difluorobenzene	−330.49	−334.51	4.02	−330.24	−0.25
1-Chloro-3,5-difluorobenzene	−338.11	−337.27	−0.84	−332.63	−5.48
2-Chloro-1,3-difluorobenzene	−314.59	−332.04	7.45	−327.86	13.26
2-Chloro-1,4-difluorobenzene	−330.49	−334.51	4.02	−330.24	−0.25
4-Chloro-1,2-difluorobenzene	−324.72	−325.52	0.79	−311.71	−13.01
1,2-Dichloro-3-fluorobenzene	−152.30	−157.23	4.94	−157.86	5.56
1,2-Dichloro-4-fluorobenzene	−165.69	−169.70	4.02	−160.25	−5.44
1,3-Dichloro-2-fluorobenzene	−148.99	−153.64	4.64	−164.68	15.69
1,3-Dichloro-5-fluorobenzene	−172.38	−168.87	−3.51	−169.45	−2.93
1,4-Dichloro-2-fluorobenzene	−164.81	−161.25	−3.56	−167.07	2.26
2,4-Dichloro-1-fluorobenzene	−164.81	−166.10	1.30	−167.07	2.26
1-Chloro-2,3,4-trifluorobenzene	−476.60	−490.99	14.39	−481.29	4.69
1-Chloro-2,3,5-trifluorobenzene	−498.90	−507.60	8.70	−502.21	3.31
1-Chloro-2,4,5-trifluorobenzene	−498.90	−512.46	13.56	−502.21	3.31
2-Chloro-1,3,4-trifluorobenzene	−487.39	−499.99	12.59	−499.82	12.43
2-Chloro-1,3,5-trifluorobenzene	−509.99	−515.26	5.27	−520.74	10.75
5-Chloro-1,2,3-trifluorobenzene	−488.31	−498.61	10.29	−483.67	−4.64
1,2-Dichloro-3,4-difluorobenzene	−325.10	−330.33	5.23	−329.82	4.73
1,2-Dichloro-3,5-difluorobenzene	−347.69	−351.79	4.10	−350.74	3.05
1,2-Dichloro-4,5-difluorobenzene	−336.81	−337.94	1.13	−332.21	−4.60
1,3-Dichloro-2,4-difluorobenzene	−332.59	−340.58	7.99	−355.18	22.59
1,3-Dichloro-2,5-difluorobenzene	−344.30	−348.19	3.89	−357.56	13.26
1,4-Dichloro-2,3-difluorobenzene	−321.71	−326.73	5.02	−336.64	14.94
1,4-Dichloro-2,5-difluorobenzene	−344.30	−348.19	3.89	−357.56	13.26
1,5-Dichloro-2,3-difluorobenzene	−333.51	−339.20	5.69	−339.03	5.52
1,5-Dichloro-2,4-difluorobenzene	−344.30	−348.19	3.89	−357.56	13.26
2,3-Dichloro-1,4-difluorobenzene	−333.88	−339.32	5.44	−348.36	14.48
2,5-Dichloro-1,3-difluorobenzene	−344.30	−348.19	3.89	−357.56	13.26
1,2,3-Trichloro-4-fluorobenzene	−172.00	−179.37	7.36	−178.36	6.36
1,2,3-Trichloro-5-fluorobenzene	−185.81	−186.98	1.17	−180.75	−5.06
1,2,4-Trichloro-3-fluorobenzene	−170.71	−175.77	5.06	−185.18	14.48
1,2,4-Trichloro-5-fluorobenzene	−182.38	−188.24	5.86	−187.57	5.19
1,2,5-Trichloro-3-fluorobenzene	−182.38	−183.38	1.00	−187.57	5.19
1,3,5-Trichloro-2-fluorobenzene	−179.12	−179.95	0.84	−194.39	15.27

TABLE 10 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2,3,4,5-tetrafluorobenzene	−649.40	−657.89	8.49	−653.25	3.85
2.Chloro-1,3,4,5-tetrafluorobenzene	−660.19	−671.74	11.55	−671.78	11.59
3-Chloro-1,2,4,5-tetrafluorobenzene	−660.19	−658.14	−2.05	−671.78	11.59
1,2-Dichloro-3,4,5-trifluorobenzene	−497.90	−503.42	5.52	−501.79	3.89
1,3-Dichloro-2,4,5-trifluorobenzene	−505.39	−513.67	8.28	−527.14	21.76
1,4-Dichloro-2,3,5-trifluorobenzene	−505.39	−513.67	8.28	−527.14	21.76
1,5-Dichloro-2,3,4-trifluorobenzene	−494.51	−499.82	5.31	−508.61	14.10
2,3-Dichloro-1,4,5-trifluorobenzene	−506.68	−517.27	10.59	−520.32	13.64
2,4-Dichloro-1,3,5-trifluorobenzene	−516.31	−516.47	0.17	−545.68	29.37
1,2,3-Trichloro-4,5-difluorobenzene	−344.80	−347.61	2.80	−350.33	5.52
1,2,4-Trichloro-3,5-difluorobenzene	−354.38	−357.86	3.47	−375.68	21.30
1,2,5-Trichloro-3,4-difluorobenzene	−343.51	−348.86	5.36	−357.15	13.64
1,3,4-Trichloro-2,5-difluorobenzene	−352.29	−357.86	5.56	−375.68	23.39
1,3,5-Trichloro-2,4-difluorobenzene	−351.00	−349.57	−1.42	−382.50	31.51
2,3,4-Trichloro-1,5-difluorobenzene	−353.51	−356.60	3.10	−368.86	15.36
1,2,3,4-Tetrachloro-5-fluorobenzene	−191.21	−191.96	0.75	−198.87	7.66
1,2,3,5-Tetrachloro-4-fluorobenzene	−190.00	−193.22	3.22	−205.69	15.69
1,2,4,5-Tetrachloro-3-fluorobenzene	−192.00	−187.02	−4.98	−205.69	13.68
Chloropentafluorobenzene	−810.40	−808.43	−1.97	−822.83	12.43
1,2-Dichlorotetrafluorobenzene	−656.89	−657.85	0.96	−671.36	14.48
1,3-Dichlorotetrafluorobenzene	−666.51	−668.10	1.59	−696.72	30.21
1,4-Dichlorotetrafluorobenzene	−666.51	−659.36	−7.15	−696.72	30.21
1,2,3-Trichlorotrifluorobenzene	−503.80	−526.97	23.18	−519.90	16.11
1,2,4-Trichlorotrifluorobenzene	−513.42	−518.48	5.06	−545.26	31.84
1,3,5-Trichlorotrifluorobenzene	−523.00	−517.85	−5.15	−570.61	47.61
1,2,3,4-Tetrachlorodifluorobenzene	−350.20	−347.73	−2.47	−368.44	18.24
1,2,3,5-Tetrachlorodifluorobenzene	−359.78	−357.98	−1.80	−393.80	34.02
1,2,4,5-Tetrachlorodifluorobenzene	−359.78	−356.64	−3.14	−393.80	34.02
Pentachlorofluorobenzene	−197.11	−195.60	−1.51	−216.98	19.87

[a] For key, see footnotes to Table 4.
[b] Also consider one half of the number of meta and para interactions between Cl and F.

TABLE 11

Entropy of chlorofluorobenzenes at 298 K, $S^{\ominus}$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	337.48	337.48	0.00	332.67	4.81
1-Chloro-3-fluorobenzene	338.11	338.11	0.00	339.41	−1.30
1-Chloro-4-fluorobenzene	332.80	332.80	0.00	333.63	−0.84
1-Chloro-2,3-difluorobenzene	356.02	356.85	−0.84	351.79	4.23
1-Chloro-2,4-difluorobenzene	356.02	356.02	0.00	351.79	4.23
1-Chloro-3,5-difluorobenzene	350.28	351.62	−1.34	352.75	−2.47
2-Chloro-1,3-difluorobenzene	350.28	350.37	−0.08	339.28	11.00
2-Chloro-1,4-difluorobenzene	356.02	356.02	0.00	351.79	4.23
4-Chloro-1,2-difluorobenzene	356.02	356.73	−0.71	358.53	−2.51
1,2-Dichloro-3-fluorobenzene	366.02	365.56	0.46	363.51	2.51
1,2-Dichloro-4-fluorobenzene	365.68	365.43	0.25	370.24	−4.56
1,3-Dichloro-2-fluorobenzene	358.90	361.20	−2.30	351,00	7.91
1,3-Dichloro-5-fluorobenzene	360.28	362.46	−2.18	364.47	−4.18
1,4-Dichloro-2-fluorobenzene	366.02	366.85	−0.84	363.51	2.51
2,4-Dichloro-1-fluorobenzene	366.02	366.85	−0.84	363.51	2.51
1-Chloro-2,3,4-trifluorobenzene	374.89	376.23	−1.34	370.91	3.97
1-Chloro-2,3,5-trifluorobenzene	374.89	376.14	−1.26	370.91	3.97

TABLE 11 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2,4,5-trifluorobenzene	374.89	375.39	−0.50	370.91	3.97
2-Chloro-1,3,4-trifluorobenzene	374.89	375.51	−0.63	364.18	10.71
2-Chloro-1,3,5-trifluorobenzene	369.11	368.19	0.92	358.40	10.71
5-Chloro-1,2,3-trifluorobenzene	369.11	371.08	−1.97	371.87	−2.76
1,2-Dichloro-3,4-difluorobenzene	384.89	385.68	−0.79	382.63	2.26
1,2-Dichloro-3,5-difluorobenzene	384.89	384.84	0.04	382.63	2.26
1,2-Dichloro-4,5-difluorobenzene	379.11	381.00	−1.88	383.59	−4.48
1,3-Dichloro-2,4-difluorobenzene	384.89	385.64	−0.75	369.15	15.73
1,3-Dichloro-2,5-difluorobenzene	379.11	380.49	−1.38	370.12	9.00
1,4-Dichloro-2,3-difluorobenzene	379.11	381.33	−2.22	370.12	9.00
1,4-Dichloro-2,5-difluorobenzene	379.11	386.27	−7.15	375.89	3.22
1,5-Dichloro-2,3-difluorobenzene	384.89	386.98	−2.09	382.63	2.26
1,5-Dichloro-2,4-difluorobenzene	373.30	380.95	−7.66	370.12	3.18
2,3-Dichloro-1,4-difluorobenzene	379.11	379.20	−0.08	370.12	9.00
2,5-Dichloro-1,3-difluorobenzene	379.11	380.49	−1.38	370.12	9.00
1,2,3-Trichloro-4-fluorobenzene	394.80	393.63	1.17	394.34	0.46
1,2,3-Trichloro-5-fluorobenzene	389.11	388.48	0.63	395.30	−6.19
1,2,4-Trichloro-3-fluorobenzene	394.80	395.05	−0.25	387.61	7.20
1,2,4-Trichloro-5-fluorobenzene	394.22	394.93	−0.71	394.34	−0.13
1,2,5-Trichloro-3-fluorobenzene	394.80	395.68	−0.88	394.34	0.46
1,3,5-Trichloro-2-fluorobenzene	389.11	391.29	−2.18	381.83	7.28
1-Chloro-2,3,4,5-tetrafluorobenzene	393.71	395.64	−1.92	390.03	3.68
2-Chloro-1,3,4,5-tetrafluorobenzene	393.71	394.17	−0.46	383.30	10.42
3-Chloro-1,2,4,5-tetrafluorobenzene	387.90	389.40	−1.51	377.52	10.38
1,2-Dichloro-3,4,5-trifluorobenzene	403.71	406.27	−2.55	401.75	1.97
1,3-Dichloro-2,4,5-trifluorobenzene	403.71	405.76	−2.05	388.28	15.44
1,4-Dichloro-2,3,5-trifluorobenzene	403.71	405.76	−2.05	388.28	15.44
1,5-Dichloro-2,3,4-trifluorobenzene	397.90	401.92	−4.02	389.24	8.66
2,3-Dichloro-1,4,5-trifluorobenzene	403.71	404.34	−0.63	395.01	8.70
2,4-Dichloro-1,3,5-trifluorobenzene	397.90	399.03	−1.13	375.77	22.13
1,2,3-Trichloro-4,5-difluorobenzene	413.71	414.97	−1.26	413.46	0.25
1,2,4-Trichloro-3,5-difluorobenzene	413.71	414.47	−0.75	399.99	13.72
1,2,5-Trichloro-3,4-difluorobenzene	413.71	415.18	−1.46	406.73	6.99
1,3,4-Trichloro-2,5-difluorobenzene	413.71	414.47	−0.75	399.99	13.72
1,3,5-Trichloro-2,4-difluorobenzene	407.90	411.29	−3.39	387.48	20.42
2,3,4-Trichloro-1,5-difluorobenzene	407.90	408.48	−0.59	400.95	6.95
1,2,3,4-Tetrachloro-5-fluorobenzene	423.59	423.17	0.42	425.18	−1.59
1,2,3,5-Tetrachloro-4-fluorobenzene	423.59	423.84	−0.25	418.44	5.15
1,2,4,5-Tetrachloro-3-fluorobenzene	417.90	418.48	−0.59	412.67	5.23
Chloropentafluorobenzene	407.69	408.90	−1.21	396.64	11.05
1,2-Dichlorotetrafluorobenzene	416.81	420.03	−3.22	408.36	8.45
1,3-Dichlorotetrafluorobenzene	416.81	419.99	−3.18	394.89	21.92
1,4-Dichlorotetrafluorobenzene	410.99	414.05	−3.05	389.15	21.84
1,2,3-Trichlorotrifluorobenzene	426.68	428.48	−1.80	420.07	6.61
1,2,4-Trichlorotrifluorobenzene	432.50	434.72	−2.22	412.38	20.13
1,3,5-Trichlorotrifluorobenzene	418.69	417.86	0.84	381.62	37.07
1,2,3,4-Tetrachlorodifluorobenzene	436.68	438.86	−2.18	431.79	4.90
1,2,3,5-Tetrachlorodifluorobenzene	436.68	438.82	−2.13	418.32	18.37
1,2,4,5-Tetrachlorodifluorobenzene	430.99	432.29	−1.30	412.58	18.41
Pentachlorofluorobenzene	446.68	445.97	0.71	443.50	3.18

[a] For key, see footnotes to Table 4.

[b] Also considers one half of the number of meta and para interactions between Cl and F.

TABLE 12

Heat capacity of chlorofluorobenzenes at 300 K, $C_p(300)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	110.29	110.29	0.00	116.23	−5.94
1-Chloro-3-fluorobenzene	110.75	110.75	0.00	111.55	−0.79
1-Chloro-4-fluorobenzene	110.83	110.83	0.00	111.55	−0.71
1-Chloro-2,3-difluorobenzene	122.84	122.51	0.33	129.03	−6.19
1-Chloro-2,4-difluorobenzene	122.84	123.18	−0.33	129.03	−6.19
1-Chloro-3,5-difluorobenzene	122.84	123.72	−0.88	124.35	−1.51
2-Chloro-1,3-difluorobenzene	122.84	122.80	0.04	133.72	−10.88
2-Chloro-1,4-difluorobenzene	122.84	123.18	−0.33	129.03	−6.19
4-Chloro-1,2-difluorobenzene	122.84	122.88	−0.04	124.35	−1.15
1,2-Dichloro-3-fluorobenzene	126.31	125.90	0.42	133.64	−7.32
1,2-Dichloro-4-fluorobenzene	126.06	126.27	−0.21	128.95	−2.89
1,3-Dichloro-2-fluorobenzene	125.69	126.36	−0.67	138.32	−12.64
1,3-Dichloro-5-fluorobenzene	126.31	127.28	−0.96	128.95	−2.64
1,4-Dichloro-2-fluorobenzene	126.31	126.73	−0.42	133.64	−7.32
2,4-Dichloro-1-fluorobenzene	126.31	126.73	−0.42	133.64	−7.32
1-Chloro-2,3,4-trifluorobenzene	134.93	134.72	0.21	141.84	−6.90
1-Chloro-2,3,5-trifluorobenzene	134.93	135.48	−0.54	141.84	−6.90
1-Chloro-2,4,5-trifluorobenzene	134.93	135.39	−0.46	141.84	−6.90
2-Chloro-1,3,4-trifluorobenzene	134.93	135.02	−0.08	146.52	−11.59
2-Chloro-1,3,5-trifluorobenzene	134.93	134.77	0.17	146.52	−11.59
5-Chloro-1,2,3-trifluorobenzene	134.93	135.19	−0.25	137.15	−2.22
1,2-Dichloro-3,4-difluorobenzene	138.41	138.20	0.21	146.44	−8.03
1,2-Dichloro-3,5-difluorobenzene	138.41	138.87	−0.46	146.44	−8.03
1,2-Dichloro-4,5-difluorobenzene	138.41	138.74	−0.33	141.75	−3.35
1,3-Dichloro-2,4-difluorobenzene	138.41	138.87	−0.46	155.81	−17.41
1,3-Dichloro-2,5-difluorobenzene	138.41	139.33	−0.92	151.13	−12.72
1,4-Dichloro-2,3-difluorobenzene	138.41	138.66	−0.25	151.13	−12.72
1,4-Dichloro-2,5-difluorobenzene	138.41	139.33	−0.92	151.13	−12.72
1,5-Dichloro-2,3-difluorobenzene	138.41	139.03	−0.63	146.44	−8.03
1,5-Dichloro-2,4-difluorobenzene	138.41	139.41	−1.00	151.13	−12.72
2,3-Dichloro-1,4-difluorobenzene	138.41	138.49	−0.08	151.13	−12.72
2,5-Dichloro-1,3-difluorobenzene	138.41	139.33	−0.92	151.13	−12.72
1,2,3-Trichloro-4-fluorobenzene	141.88	141.50	0.38	151.04	−9.16
1,2,3-Trichloro-5-fluorobenzene	141.88	141.96	−0.08	146.36	−4.48
1,2,4-Trichloro-3-fluorobenzene	141.88	141.96	−0.08	155.73	−13.85
1,2,4-Trichloro-5-fluorobenzene	141.59	142.34	−0.75	151.04	−9.46
1,2,5-Trichloro-3-fluorobenzene	141.88	142.42	−0.54	151.04	−9.16
1,3,5-Trichloro-2-fluorobenzene	141.88	142.30	−0.42	155.73	−13.85
1-Chloro-2,3,4,5-tetrafluorobenzene	147.03	146.11	0.92	154.64	−7.61
2-Chloro-1,3,4,5-tetrafluorobenzene	147.03	146.31	0.71	159.33	−12.30
3-Chloro-1,2,4,5-tetrafluorobenzene	147.03	146.15	0.88	159.33	−12.30
1,2-Dichloro-3,4,5-trifluorobenzene	150.50	150.58	−0.08	159.24	−8.74
1,3-Dichloro-2,4,5-trifluorobenzene	150.50	151.17	−0.67	168.62	−18.12
1,4-Dichloro-2,3,5-trifluorobenzene	150.50	151.17	−0.67	168.62	−18.12
1,5-Dichloro-2,3,4-trifluorobenzene	150.50	151.04	−0.54	163.93	−13.43
2,3-Dichloro-1,4,5-trifluorobenzene	150.50	150.71	−0.21	163.93	−13.43
2,4-Dichloro-1,3,5-trifluorobenzene	150.50	150.62	−0.13	173.30	−22.80
1,2,3-Trichloro-4,5-difluorobenzene	153.97	153.97	0.00	163.85	−9.87
1,2,4-Trichloro-3,5-difluorobenzene	153.97	154.56	−0.59	173.22	−19.25
1,2,5-Trichloro-3,4-difluorobenzene	153.97	154.26	−0.29	168.53	−14.56
1,3,4-Trichloro-2,5-difluorobenzene	153.97	154.56	−0.59	173.22	−19.25

TABLE 12 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1,3,5-Trichloro-2,4-difluorobenzene	153.97	154.60	−0.63	177.90	−23.93
2,3,4-Trichloro-1,5-difluorobenzene	153.97	154.26	−0.29	168.53	−14.56
1,2,3,4-Tetrachloro-5-fluorobenzene	157.44	156.69	0.75	168.45	−11.00
1,2,3,5-Tetrachloro-4-fluorobenzene	157.44	157.07	0.38	173.13	−15.69
1,2,4,5-Tetrachloro-3-fluorobenzene	157.44	156.73	0.71	173.13	−15.69
Chloropentafluorobenzene	158.95	156.77	2.18	172.13	−13.18
1,2-Dichlorotetrafluorobenzene	162.59	161.59	1.00	176.73	−14.14
1,3-Dichlorotetrafluorobenzene	162.59	162.26	0.33	186.10	−23.51
1,4-Dichlorotetrafluorobenzene	162.59	161.92	0.67	186.10	−23.51
1,2,3-Trichlorotrifluorobenzene	166.06	165.73	0.33	181.33	−15.27
1,2,4-Trichlorotrifluorobenzene	166.06	166.48	−0.42	190.71	−24.64
1,3,5-Trichlorotrifluorobenzene	165.39	165.81	−0.42	200.08	−34.69
1,2,3,4-Tetrachlorodifluorobenzene	169.54	168.78	0.75	185.94	−16.40
1,2,3,5-Tetrachlorodifluorobenzene	169.54	169.45	0.08	195.31	−25.77
1,2,3,5-Tetrachlorodifluorobenzene	169.54	168.95	0.59	195.31	−25.77
Pentachlorofluorobenzene	173.01	171.00	2.01	190.54	−17.53

[a] For key, see footnotes to Table 4.
[b] Also considers on half of the number of meta and para interactions between Cl and F.

TABLE 13

Heat capacity of chlorofluorobenzenes at 500 K, $C_p(500)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	163.39	163.39	0.00	170.87	−7.49
1-Chloro-3-fluorobenzene	163.97	163.97	0.00	165.44	−1.46
1-Chloro-4-fluorobenzene	163.89	163.89	0.00	165.44	−1.55
1-Chloro-2,3-difluorobenzene	174.56	174.31	0.25	183.59	−9.04
1-Chloro-2,4-difluorobenzene	174.56	177.11	−2.55	183.59	−9.04
1-Chloro-3,5-difluorobenzene	174.56	175.39	−0.84	178.15	−3.60
2-Chloro-1,3-difluorobenzene	174.56	174.22	0.33	189.03	−14.48
2-Chloro-1,4-difluorobenzene	174.56	177.11	−2.55	183.59	−9.04
4-Chloro-1,2-difluorobenzene	174.56	177.19	−2.64	178.15	−3.60
1,2-Dichloro-3-fluorobenzene	177.15	176.90	0.25	186.52	−9.37
1,2-Dichloro-4-fluorobenzene	177.15	179.79	−2.64	181.08	−3.93
1,3-Dichloro-2-fluorobenzene	176.98	175.98	1.00	191.96	−14.98
1,3-Dichloro-5-fluorobenzene	177.15	177.15	0.00	181.08	−3.93
1,4-Dichloro-2-fluorobenzene	177.15	176.56	0.59	186.52	−9.37
2,4-Dichloro-1-fluorobenzene	177.15	178.87	−1.72	186.52	−9.37
1-Chloro-2,3,4-trifluorobenzene	185.43	185.23	0.21	196.31	−10.88
1-Chloro-2,3,5-trifluorobenzene	185.43	185.73	−0.29	196.31	−10.88
1-Chloro-2,4,5-trifluorobenzene	185.43	188.03	−2.59	196.31	−10.88
2-Chloro-1,3,4-trifluorobenzene	185.43	185.14	0.29	201.75	−16.32
2-Chloro-1,3,5-trifluorobenzene	185.43	184.72	0.71	201.75	−16.32
5-Chloro-1,2,3-trifluorobenzene	185.43	185.81	−0.38	190.87	−5.44
1,2-Dichloro-3,4-difluorobenzene	188.03	185.52	2.51	199.24	−11.21
1,2-Dichloro-3,5-difluorobenzene	188.03	188.32	−0.29	199.24	−11.21
1,2-Dichloro-4,5-difluorobenzene	188.03	186.02	2.01	193.80	−5.77
1,3-Dichloro-2,4-difluorobenzene	188.03	186.82	1.21	210.12	−22.09
1,3-Dichloro-2,5-difluorobenzene	188.03	187.40	0.63	204.68	−16.65
1,4-Dichloro-2,3-difluorobenzene	188.03	184.60	3.43	204.68	−16.65

TABLE 13 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1,4-Dichloro-2,5-difluorobenzene	188.03	187.40	0.63	204.68	−16.65
1,5-Dichloro-2,3-difluorobenzene	188.03	187.49	0.54	199.24	−11.21
1,5-Dichloro-2,4-difluorobenzene	188.03	187.32	0.71	204.68	−16.65
2,3-Dichloro-1,4-difluorobenzene	188.03	185.43	2.59	204.68	−16.65
2,5-Dichloro-1,3-difluorobenzene	188.03	187.40	0.63	204.68	−16.65
1,2,3-Trichloro-4-fluorobenzene	190.62	190.41	0.21	202.17	−11.55
1,2,3-Trichloro-5-fluorobenzene	190.62	191.00	−0.38	196.73	−6.11
1,2,4-Trichloro-3-fluorobenzene	190.62	189.49	1.13	207.61	−16.99
1,2,4-Trichloro-5-fluorobenzene	190.46	192.38	−1.92	202.17	−11.72
1,2,5-Trichloro-3-fluorobenzene	190.62	190.08	0.54	202.17	−11.55
1,3,5-Trichloro-2-fluorobenzene	190.62	189.91	0.71	207.61	−16.99
1-Chloro-2,3,4,5-tetrafluorobenzene	196.31	190.62	5.69	209.03	−12.72
2-Chloro-1,3,4,5-tetrafluorobenzene	196.31	192.84	3.47	214.47	−18.16
3-Chloro-1,2,4,5-tetrafluorobenzene	196.31	187.69	8.62	214.47	−18.16
1,2-Dichloro-3,4,5-trifluorobenzene	198.91	194.05	4.85	211.96	−13.05
1,3-Dichloro-2,4,5-trifluorobenzene	198.91	195.43	3.47	222.84	−23.93
1,4-Dichloro-2,3,5-trifluorobenzene	198.91	195.43	3.47	222.84	−23.93
1,5-Dichloro-2,3,4-trifluorobenzene	198.91	193.13	5.77	217.40	−18.49
2,3-Dichloro-1,4,5-trifluorobenzene	198.91	196.36	2.55	217.40	−18.49
2,4-Dichloro-1,3,5-trifluorobenzene	198.91	192.05	6.86	228.28	−29.37
1,2,3-Trichloro-4,5-difluorobenzene	201.50	196.65	4.85	214.89	−13.39
1,2,4-Trichloro-3,5-difluorobenzene	201.50	198.03	3.47	225.77	−24.27
1,2,5-Trichloro-3,4-difluorobenzene	201.50	198.11	3.39	220.33	−18.83
1,3,4-Trichloro-2,5-difluorobenzene	201.50	198.03	3.47	225.77	−24.27
1,3,5-Trichloro-2,4-difluorobenzene	201.50	195.48	6.02	231.21	−29.71
2,3,4-Trichloro-1,5-difluorobenzene	201.50	196.56	4.94	220.33	−18.83
1,2,3,4-Tetrachloro-5-fluorobenzene	204.10	200.08	4.02	217.82	−13.72
1,2,3,5-Tetrachloro-4-fluorobenzene	204.10	201.46	2.64	223.26	−19.16
1,2,4,5-Tetrachloro-3-fluorobenzene	204.10	197.57	6.53	223.26	−19.16
Chloropentafluorobenzene	205.60	192.59	13.01	227.19	−21.59
1,2-Dichlorotetrafluorobenzene	209.79	196.56	13.22	230.12	−20.33
1,3-Dichlorotetrafluorobenzene	209.79	197.86	11.92	241.00	−31.21
1,4-Dichlorotetrafluorobenzene	209.79	195.10	14.69	241.00	−31.21
1,2,3-Trichlorotrifluorobenzene	212.38	204.93	7.45	233.05	−20.67
1,2,4-Trichlorotrifluorobenzene	212.38	203.76	8.62	243.93	−31.55
1,3,5-Trichlorotrifluorobenzene	210.87	200.20	10.67	254.81	−43.93
1,2,3,4-Tetrachlorodifluorobenzene	214.97	203.43	11.55	235.98	−21.00
1,2,3,5-Tetrachlorodifluorobenzene	214.97	204.72	10.25	246.86	−31.88
1,2,4,5-Tetrachlorodifluorobenzene	214.97	203.22	11.76	246.86	−31.88
Pentachlorofluorobenzene	217.57	207.57	10.00	238.91	−21.34

[a] For key, see footnotes to Table 4.
[b] Also considers one half of the number of meta and para interactions between Cl and F.

TABLE 14

Heat capacity of chlorofluorobenzenes at 800 K, $C_p(800)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	208.82	208.82	0.00	213.55	−4.73
1-Chloro-3-fluorobenzene	209.12	209.12	0.00	209.87	−0.75
1-Chloro-4-fluorobenzene	209.16	209.16	0.00	209.87	−0.71

TABLE 14 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2,3-difluorobenzene	217.48	218.28	−0.79	223.01	−5.52
1-Chloro-2,4-difluorobenzene	217.48	220.29	−2.80	223.01	−5.52
1-Chloro-3,5-difluorobenzene	217.48	217.23	0.25	219.33	−1.84
2-Chloro-1,3-difluorobenzene	217.48	216.65	0.84	226.69	−9.20
2-Chloro-1,4-difluorobenzene	217.48	220.29	−2.80	223.01	−5.52
4-Chloro-1,2-difluorobenzene	217.48	221.92	−4.44	219.33	−1.84
1,2-Dichloro-3-fluorobenzene	218.95	218.70	0.25	224.68	−5.73
1,2-Dichloro-4-fluorobenzene	219.16	222.34	−3.18	221.00	−1.84
1,3-Dichloro-2-fluorobenzene	219.07	216.90	2.18	228.36	−9.29
1,3-Dichloro-5-fluorobenzene	218.95	217.48	1.46	221.00	−2.05
1,4-Dichloro-2-fluorobenzene	218.95	220.54	−1.59	224.68	−5.73
2,4-Dichloro-1-fluorobenzene	218.95	220.54	−1.59	224.68	−5.73
1-Chloro-2,3,4-trifluorobenzene	225.98	227.74	−1.76	232.46	−6.49
1-Chloro-2,3,5-trifluorobenzene	225.98	226.40	−0.42	232.46	−6.49
1-Chloro-2,4,5-trifluorobenzene	225.98	229.74	−3.77	232.46	−6.49
2-Chloro-1,3,4-trifluorobenzene	225.98	226.10	−0.13	236.14	−10.17
2-Chloro-1,3,5-trifluorobenzene	225.98	224.22	1.76	236.14	−10.17
5-Chloro-1,2,3-trifluorobenzene	225.98	228.03	−2.05	228.78	−2.80
1,2-Dichloro-3,4-difluorobenzene	227.44	224.81	2.64	234.14	−6.69
1,2-Dichloro-3,5-difluorobenzene	227.44	226.81	0.63	234.14	−6.69
1,2-Dichloro-4,5-difluorobenzene	227.44	225.14	2.30	230.45	−3.01
1,3-Dichloro-2,4-difluorobenzene	227.44	224.72	2.72	241.50	−14.06
1,3-Dichloro-2,5-difluorobenzene	227.44	225.02	2.43	237.82	−10.38
1,4-Dichloro-2,3-difluorobenzene	227.44	223.01	4.44	237.82	−10.38
1,4-Dichloro-2,5-difluorobenzene	227.44	225.02	2.43	237.82	−10.38
1,5-Dichloro-2,3-difluorobenzene	227.44	226.65	0.79	234.14	−6.69
1,5-Dichloro-2,4-difluorobenzene	227.44	225.06	2.38	237.82	−10.38
2,3-Dichloro-1,4-difluorobenzene	227.44	223.17	4.27	237.82	−10.38
2,5-Dichloro-1,3-difluorobenzene	227.44	225.02	2.43	237.82	−10.38
1,2,3-Trichloro-4-fluorobenzene	228.91	228.57	0.33	235.81	−6.90
1,2,3-Trichloro-5-fluorobenzene	228.91	228.86	0.04	232.13	−3.22
1,2,4-Trichloro-3-fluorobenzene	228.91	226.77	2.13	239.49	−10.59
1,2,4-Trichloro-5-fluorobenzene	229.12	230.41	−1.30	235.81	−6.69
1,2,5-Trichloro-3-fluorobenzene	228.91	227.07	1.84	235.81	−6.90
1,3,5-Trichloro-2-fluorobenzene	228.91	226.81	2.09	239.49	−10.59
1-Chloro-2,3,4,5-tetrafluorobenzene	234.47	229.95	4.52	241.92	−7.45
2-Chloro-1,3,4,5-tetrafluorobenzene	234.47	231.67	2.80	245.60	−11.13
3-Chloro-1,2,4,5-tetrafluorobenzene	234.47	224.47	10.00	245.60	−11.13
1,2-Dichloro-3,4,5-trifluorobenzene	235.94	230.96	4.98	243.59	−7.66
1,3-Dichloro-2,4,5-trifluorobenzene	235.94	230.83	5.10	250.96	−15.02
1,4-Dichloro-2,3,5-trifluorobenzene	235.94	230.83	5.10	250.96	−15.02
1,5-Dichloro-2,3,4-trifluorobenzene	235.94	229.16	6.78	247.27	−11.34
2,3-Dichloro-1,4,5-trifluorobenzene	235.94	232.63	3.31	247.27	−11.34
2,4-Dichloro-1,3,5-trifluorobenzene	235.94	225.35	10.59	254.64	−18.70
1,2,3-Trichloro-4,5-difluorobenzene	237.40	231.38	6.02	245.27	−7.87
1,2,4-Trichloro-3,5-difluorobenzene	237.40	231.25	6.15	252.63	−15.23
1,2,5-Trichloro-3,4-difluorobenzene	237.40	232.88	4.52	248.95	−11.55
1,3,4-Trichloro-2,5-difluorobenzene	237.40	231.25	6.15	252.63	−15.23
1,3,5-Trichloro-2,4-difluorobenzene	237.40	227.69	9.71	256.31	−18.91
2,3,4-Trichloro-1,5-difluorobenzene	237.40	229.74	7.66	248.95	−11.55
1,2,3,4-Tetrachloro-5-fluorobenzene	238.86	233.30	5.56	246.94	−8.08
1,2,3,5-Tetrachloro-4-fluorobenzene	238.86	234.85	4.02	250.62	−11.76
1,2,4,5-Tetrachloro-3-fluorobenzene	238.86	229.95	8.91	250.62	−11.76

TABLE 14 (continued)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
Chloropentafluorobenzene	242.09	228.03	14.06	255.06	−12.97
1,2-Dichlorotetrafluorobenzene	244.43	229.53	14.90	256.73	−12.30
1,3-Dichlorotetrafluorobenzene	244.43	229.45	14.98	264.09	−19.66
1,4-Dichlorotetrafluorobenzene	244.43	225.56	18.87	264.09	−19.66
1,2,3-Trichlorotrifluorobenzene	245.89	237.23	8.66	258.40	−12.51
1,2,4-Trichlorotrifluorobenzene	245.89	233.72	12.18	265.77	−19.87
1,3,5-Trichlorotrifluorobenzene	245.39	227.99	17.41	273.13	−27.74
1,2,3,4-Tetrachlorodifluorobenzene	247.36	232.46	14.90	260.08	−12.72
1,2,3,5-Tetrachlorodifluorobenzene	247.36	232.38	14.98	267.44	−20.08
1,2,4,5-Tetrachlorodifluorobenzene	247.36	230.79	16.57	267.44	−20.08
Pentachlorofluorobenzene	248.82	236.19	12.64	261.75	−12.93

[a] For key, see footnotes to Table 4.
[b] Also considers one half of the number of meta and para interactions between Cl and F.

TABLE 15

Heat capacity of chlorofluorobenzenes at 1000 K, $C_p(1000)$ in J mol^{-1} K^{-1} [a]

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1-Chloro-2-fluorobenzene	226.52	226.52	0.00	229.70	−3.18
1-Chloro-3-fluorobenzene	226.73	226.73	0.00	226.94	−0.21
1-Chloro-4-fluorobenzene	226.77	226.77	0.00	226.94	−0.17
1-Chloro-2,3-difluorobenzene	233.80	235.27	−1.46	237.19	−3.39
1-Chloro-2,4-difluorobenzene	233.80	236.44	−2.64	237.19	−3.39
1-Chloro-3,5-difluorobenzene	233.80	232.84	0.96	234.43	−0.63
2-Chloro-1,3-difluorobenzene	233.80	232.42	1.38	239.95	−6.15
2-Chloro-1,4-difluorobenzene	233.80	236.44	−2.64	237.19	−3.39
4-Chloro-1,2-difluorobenzene	233.80	239.28	−5.48	234.43	−0.63
1,2-Dichloro-3-fluorobenzene	234.89	234.43	0.46	238.03	−3.14
1,2-Dichloro-4-fluorobenzene	234.97	238.45	−3.47	235.27	−0.29
1,3-Dichloro-2-fluorobenzene	234.93	232.00	2.93	240.79	−5.86
1,3-Dichloro-5-fluorobenzene	234.89	232.42	2.47	235.27	−0.38
1,4-Dichloro-2-fluorobenzene	234.89	236.02	−1.13	238.03	−3.14
2,4-Dichloro-1-fluorobenzene	234.89	236.02	−1.13	238.03	−3.14
1-Chloro-2,3,4-trifluorobenzene	240.91	244.01	−3.10	244.68	−3.77
1-Chloro-2,3,5-trifluorobenzene	240.91	241.37	−0.46	244.68	−3.77
1-Chloro-2,4,5-trifluorobenzene	240.91	245.18	−4.27	244.68	−3.77
2-Chloro-1,3,4-trifluorobenzene	240.91	241.17	−0.25	247.44	−6.53
2-Chloro-1,3,5-trifluorobenzene	240.91	237.90	3.01	247.44	−6.53
5-Chloro-1,2,3-trifluorobenzene	240.91	244.22	−3.31	241.92	−1.00
1,2-Dichloro-3,4-difluorobenzene	242.00	239.37	2.64	245.52	−3.51
1,2-Dichloro-3,5-difluorobenzene	242.00	240.54	1.46	245.52	−3.51
1,2-Dichloro-4,5-difluorobenzene	242.00	239.62	2.38	242.76	−0.75
1,3-Dichloro-2,4-difluorobenzene	242.00	237.90	4.10	251.04	−9.04
1,3-Dichloro-2,5-difluorobenzene	242.00	238.11	3.89	248.28	−6.28
1,4-Dichloro-2,3-difluorobenzene	242.00	236.94	5.06	248.28	−6.28
1,4-Dichloro-2,5-difluorobenzene	242.00	238.11	3.89	248.28	−6.28
1,5-Dichloro-2,3-difluorobenzene	242.00	240.96	1.05	245.52	−3.51
1,5-Dichloro-2,4-difluorobenzene	242.00	238.15	3.85	248.28	−6.28
2,3-Dichloro-1,4-difluorobenzene	242.00	236.52	5.48	248.28	−6.28
2,5-Dichloro-1,3-difluorobenzene	242.00	238.11	3.89	248.28	−6.28

TABLE 15 (*Continued.*)

Species	Ref. 21	THERM [b]	DEV	BENSON	DEV-B
1,2,3-Trichloro-4-fluorobenzene	243.09	242.34	0.75	246.35	−3.26
1,2,3-Trichloro-5-fluorobenzene	243.09	242.55	0.54	243.59	−0.50
1,2,4-Trichloro-3-fluorobenzene	243.09	239.91	3.18	249.12	−6.02
1,2,4-Trichloro-5-fluorobenzene	243.13	243.93	−0.79	246.35	−3.22
1,2,5-Trichloro-3-fluorobenzene	243.09	240.12	2.97	246.35	−3.26
1,3,5-Trichloro-2-fluorobenzene	243.09	239.91	3.18	249.12	−6.02
1-Chloro-2,3,4,5-tetrafluorobenzene	248.03	244.51	3.51	252.17	−4.14
2-Chloro-1,3,4,5-tetrafluorobenzene	248.03	245.48	2.55	254.93	−6.90
3-Chloro-1,2,4,5-tetrafluorobenzene	248.03	237.44	10.59	254.93	−6.90
1,2-Dichloro-3,4,5-trifluorobenzene	249.12	244.35	4.77	253.01	−3.89
1,3-Dichloro-2,4,5-trifluorobenzene	249.12	242.84	6.28	258.53	−9.41
1,4-Dichloro-2,3,5-trifluorobenzene	249.12	242.84	6.28	258.53	−9.41
1,5-Dichloro-2,3,4-trifluorobenzene	249.12	241.92	7.20	255.77	−6.65
2,3-Dichloro-1,4,5-trifluorobenzene	249.12	245.27	3.85	255.77	−6.65
2,4-Dichloro-1,3,5-trifluorobenzene	249.12	235.60	13.51	261.29	−12.18
1,2,3-Trichloro-4,5-difluorobenzene	250.20	243.51	6.69	253.84	−3.64
1,2,4-Trichloro-3,5-difluorobenzene	250.20	242.00	8.20	259.37	−9.16
1,2,5-Trichloro-3,4-difluorobenzene	250.20	244.85	5.36	256.60	−6.40
1,3,4-Trichloro-2,5-difluorobenzene	250.20	242.00	8.20	259.37	−9.16
1,3,5-Trichloro-2,4-difluorobenzene	250.20	238.03	12.18	262.13	−11.92
2,3,4-Trichloro-1,5-difluorobenzene	250.20	240.66	9.54	256.60	−6.40
1,2,3,4-Tetrachloro-5-fluorobenzene	251.29	244.85	6.44	254.68	−3.39
1,2,3,5-Tetrachloro-4-fluorobenzene	251.29	246.23	5.06	257.44	−6.15
1,2,4,5-Tetrachloro-3-fluorobenzene	251.29	240.83	10.46	257.44	−6.15
Chloropentafluorobenzene	254.43	240.58	13.85	262.42	−7.99
1,2-Dichlorotetrafluorobenzene	256.23	240.83	15.40	263.26	−7.03
1,3-Dichlorotetrafluorobenzene	256.23	239.37	16.86	268.78	−12.55
1,4-Dichlorotetrafluorobenzene	256.23	235.10	21.13	268.78	−12.55
1,2,3-Trichlorotrifluorobenzene	257.32	248.03	9.29	264.09	−6.78
1,2,4-Trichlorotrifluorobenzene	257.32	242.92	14.39	269.62	−12.30
1,3,5-Trichlorotrifluorobenzene	256.86	235.48	21.38	275.14	−18.28
1,2,3,4-Tetrachlorodifluorobenzene	258.40	242.00	16.40	264.93	−6.53
1,2,3,5-Tetrachlorodifluorobenzene	258.40	240.54	17.87	270.45	−12.05
1,2,4,5-Tetrachlorodifluorobenzene	258.40	238.91	19.50	270.45	−12.05
Pentachlorofluorobenzene	259.49	245.56	13.93	265.77	−6.28

[a] For key, see footnotes to Table 4.
[b] Also considers one half of the number of meta and para interactions between Cl and F.

We have also considered separately the recently improved hydrocarbon group values reported by Cohen [23] and have determined an additional set of CH_3/CH_3 and CH_3/OH interaction groups based on these hydrocarbon groups. The data set in Table 16 compares the literature values with the calculation results using Benson groups, and using the group values based on Cohen [23]. THERM-C and DEV-C denote the respective calculation results and deviations when the values of the CH_3/CH_3 and CH_3/OH interaction groups were determined from Cohen's hydrocarbon group values.

Table 16a lists the heats of formation for methylbenzenes and methyl-

TABLE 16a

Enthalpy of formation at 298 K, $\Delta_f H^{\ominus}$ in kJ mol^{-1}

Species	Ref. 21	THERM [a]	DEV [b]	THERM-C [c]	DEV-C	BENSON [a]	DEV-B [f]
Toluene	50.00	49.41	0.59	50.58	−0.59	49.41	0.59
o-Xylene	19.08	19.08	0.00	19.08	0.00	18.37	0.71
m-Xylene	17.32	17.32	0.00	17.32	0.00	15.98	1.34
p-Xylene	18.03	18.03	0.00	18.03	0.00	15.98	2.05
1,2,3-Trimethylbenzene	−9.50	−9.50	0.00	−7.32	−2.18	−12.68	3.18
1,2,4-Trimethylbenzene	−13.81	−14.35	0.54	−13.05	−0.75	−15.06	1.26
1,3,5-Trimethylbenzene	−15.90	−13.43	−2.47	−16.82	0.92	−17.45	1.55
1,2,3,4-Tetramethylbenzene [g]	−36.02	−36.74	0.71	−34.73	−1.30	−43.72	7.70
1,2,3,5-Tetramethylbenzene [g]	−43.18	−41.59	−1.59	−40.58	−2.59	−46.11	2.93
1,2,4,5-Tetramethylbenzene [g]	−46.90	−41.30	−5.61	−45.98	−0.92	−46.11	−0.79
Pentamethylbenzene [g]	−62.43	−61.92	−0.50	−62.43	0.00	−74.77	12.34
Hexamethylbenzene [g]	−78.62	−82.55	3.93	−78.87	0.25	−103.43	24.81
Phenol	−96.40	−93.30	−3.10	−96.36	−0.04	−93.30	−3.10
o-Cresol	−128.57	−128.57	0.00	−128.57	0.00	−124.35	−4.23
m-Cresol	−132.30	−128.11	−4.18	−128.45	−3.85	−126.73	−5.56
p-Cresol	−125.35	−125.35	0.00	−125.35	0.00	−126.73	1.38
2,3-Xylenol	−157.19	−160.16	2.97	−159.91	2.72	−155.39	−1.80
2,4-Xylenol	−162.88	−159.24	−3.64	−158.57	−4.31	−157.78	−5.10
2,5-Xylenol	−161.63	−161.34	−0.29	−160.96	−0.67	−157.78	−3.85
2,6-Xylenol	−161.75	−162.51	0.75	−161.80	0.04	−155.39	−6.36
3,4-Xylenol	−156.57	−157.07	0.50	−157.74	1.17	−157.78	1.21
3,5-Xylenol	−161.54	−161.59	0.04	−161.54	0.00	−160.16	−1.38

TABLE 16b

Entropy at 298 K, $S^{\ominus}$ in J mol^{-1} K^{-1}

Species	Ref. 21	THERM	DEV	THERM-C	DEV-C	BENSON	DEV-B
Phenol	314.80	314.51	0.29	315.18	−0.38	314.51	0.29
o-Cresol	352.59	357.61	−5.02	357.94	−5.36	351.25	1.34
m-Cresol	356.06	358.61	−2.55	358.95	−2.89	357.98	−1.92
p-Cresol	350.74	350.74	0.00	350.74	0.00	352.21	−1.46
2,3-Xylenol	390.07	391.50	−1.42	391.50	−1.42	382.17	7.91
2,4-Xylenol	397.73	394.34	3.39	394.01	3.72	388.90	8.83
2,5-Xylenol	395.76	396.94	−1.17	396.94	−1.17	388.90	6.86
2,6-Xylenol	389.74	389.70	0.04	389.70	0.04	376.43	13.31
3,4-Xylenol	391.16	390.41	0.75	390.07	1.09	388.90	2.26
3,5-Xylenol	391.71	391.71	0.00	391.71	0.00	389.91	1.80

TABLE 16c

Heat capacity at 300 K, $C_p(300)$ in J mol^{-1} K^{-1}

Species	Ref. 21	THERM	DEV	THERM-C	DEV-C	BENSON	DEV-B
Phenol	103.85	102.09	1.76	103.34	0.50	102.09	1.76
o-Cresol	127.99	130.42	−2.43	131.04	−3.05	130.29	−2.30
m-Cresol	125.39	128.78	−3.39	129.41	−4.02	125.60	−0.21
p-Cresol	125.69	125.69	0.00	125.69	0.00	125.60	0.08
2,3-Xylenol	164.89	161.75	3.14	161.75	3.14	158.49	6.40
2,4-Xylenol	156.94	152.09	4.85	151.46	5.48	153.80	3.14
2,5-Xylenol	157.90	155.52	2.38	155.52	2.38	153.80	4.10
2,6-Xylenol	156.77	156.82	−0.04	156.82	−0.04	158.49	−1.72
3,4-Xylenol	164.35	157.03	7.32	156.40	7.95	153.80	10.54
3,5-Xylenol	153.51	153.55	−0.04	153.55	−0.04	149.12	4.39

TABLE 16d

Heat capacity at 500 K, $C_p(500)$ in J mol^{-1} K^{-1}

Species	Ref. 21	THERM	DEV	THERM-C	DEV-C	BENSON	DEV-B
Phenol	161.92	160.33	1.59	161.75	0.17	160.25	1.67
o-Cresol	195.31	197.07	−1.76	197.78	−2.47	197.57	−2.26
m-Cresol	194.56	196.61	−2.05	197.32	−2.76	192.13	2.43
p-Cresol	194.01	194.01	0.00	194.01	0.00	192.13	1.88
2,3-Xylenol	240.41	236.81	3.60	236.81	3.60	234.89	5.52
2,4-Xylenol	235.85	231.71	4.14	231.00	4.85	229.45	6.40
2,5-Xylenol	236.27	235.81	0.46	235.81	0.46	229.45	6.82
2,6-Xylenol	234.72	234.76	−0.04	234.76	−0.04	234.89	−0.17
3,4-Xylenol	240.96	233.76	7.20	233.05	7.91	229.45	11.51
3,5-Xylenol	233.80	233.84	−0.04	233.84	−0.04	224.01	9.79

TABLE 16e

Heat capacity at 800 K, $C_p(800)$ in J mol^{-1} K^{-1}

Species	Ref. 21	THERM	DEV	THERM-C	DEV-C	BENSON	DEV-B
Phenol	212.13	211.79	0.33	212.51	−0.38	211.71	0.42
o-Cresol	257.69	260.24	−2.55	260.62	−2.93	259.07	−1.38
m-Cresol	257.32	260.29	−2.97	260.66	−3.35	255.39	1.92
p-Cresol	256.69	256.69	0.00	256.69	0.00	255.39	1.30
2,3-Xylenol	312.84	310.41	2.43	310.45	2.38	306.44	6.40
2,4-Xylenol	310.41	305.98	4.44	305.64	4.77	302.75	7.66
2,5-Xylenol	310.83	310.95	−0.13	311.00	−0.17	302.75	8.08
2,6-Xylenol	309.87	309.53	0.33	309.57	0.29	306.44	3.43
3,4-Xylenol	313.01	306.85	6.15	306.52	6.49	302.75	10.25
3,5-Xylenol	309.62	309.62	0.00	309.66	−0.04	299.07	10.54

TABLE 16f

Heat capacity at 1000 K, $C_p(1000)$ in J mol^{-1} K^{-1}

Species	Ref. 21	THERM	DEV	THERM-C	DEV-C	BENSON	DEV-B
Phenol	232.50	232.46	0.04	233.26	−0.75	232.42	0.08
o-Cresol	283.72	286.44	−2.72	287.11	−3.39	284.55	−0.84
m-Cresol	283.34	286.81	−3.47	287.23	−3.89	281.79	1.55
p-Cresol	282.84	282.84	0.00	282.84	0.00	281.79	1.05
2,3-Xylenol	343.80	342.00	1.80	342.29	1.51	336.69	7.11
2,4-Xylenol	342.08	337.27	4.81	337.15	4.94	333.93	8.16
2,5-Xylenol	342.46	342.33	0.13	342.63	−0.17	333.93	8.54
2,6-Xylenol	341.41	340.87	0.54	341.41	0.00	336.69	4.73
3,4-Xylenol	343.84	338.40	5.44	338.03	5.82	333.93	9.92
3,5-Xylenol	341.62	341.62	0.00	341.67	−0.04	331.16	10.46

[a] THERM: Calculation results from this work. [b] DEV: deviation between the literature values and the results from this study. [c] THERM-C: calculation results when the values of the CH_3/CH_3 and CH_3/OH interaction groups were determined from Cohen's hydrocarbon group values [23]. [d] DEV-C: deviations when the values of the CH_3/CH_3 and CH_3/OH interaction groups were determined from Cohen's hydrocarbon group values [23]. [e] BENSON: calculation results using Benson's group calculations which include only ortho interactions. [f] DEV-B: deviation between the literature values and the results from Benson's group calculations. [g] Data from ref. 24.

phenols. Tables 16b–16f give comparisons of the literature values and calculation results of the entropies and heat capacities for methylphenols.

Table 17 summarizes the overall deviations for each class of compound resulting from the estimation results derived here and from using Benson's

TABLE 17

Absolute average deviation for the enthalpy of formation $\Delta_f H^{\ominus}(298)$ in kJ mol^{-1}, entropy $S^{\ominus}(298)$ in J mol^{-1} K^{-1}, and heat capacities $C_p(300)$, $C_p(500)$, $C_p(800)$, $C_p(1000)$ in J mol^{-1} K^{-1}

Compound classes	$\Delta H_f^{\ominus}(298)$		$S^{\ominus}(298)$		$C_p(300)$		$C_p(500)$		$C_p(800)$		$C_p(1000)$	
	THERM	BENSON	THERM	BENSON	THERM	BENSON	THERM	BENSON	THERM	BENSON	THERM	BENSON
F-Bzs	5.21	7.1	1.03	1.04	1.28	0.87	2.90	3.85	3.27	1.96	3.70	1.02
Cl-Bzs	2.12	2.61	0.66	6.44	0.84	4.42	1.51	4.95	2.02	2.36	1.99	0.13
Br-Bzs	2.16	6.53	2.29	4.16	1.00	11.71	3.37	13.22	0.53	7.96	1.75	4.72
CH_3-Bzs	1.33 [a] 0.79 [b]	4.94	2.02	3.19	3.17	3.16	1.91	3.17	2.17	2.67	1.30	1.98
CH_3-Phenols	1.55 [a] 1.28 [b]	3.40	1.46 [a] 1.61 [b]	4.60	2.54 [a] 2.66 [b]	3.46	2.09 [a] 2.23 [b]	4.85	1.93 [a] 2.08 [b]	5.14	1.90 [a] 2.05 [b]	5.24
Cl-F-Bzs	4.92	12.87	1.42	7.91	0.49	12.12	3.69	16.14	5.06	9.91	5.98	5.76
Cl-Biphenyls	2.73	4.09	2.85	10.10	1.31	5.47	0.91	7.43	1.47	2.91	1.70	1.56

[a] Average deviations from those group values based on hydrocarbons groups in Benson [3].
[b] Average deviations from those group values based on hydrocarbons groups in Cohen [23].

groups only. One can see that use of the interaction terms yields data which are closer to the experimental values than with Benson's groups alone, especially for the important parameters $\Delta_f H^{\ominus}$ and $S^{\ominus}$. There are only two data sets for $C_p(300)$ and $C_p(1000)$ of flurobenzenes, where Benson's group values yield slightly better results. We note that it is not surprising that use of these interaction terms provides better overall results, because we have added more parameters in the calculation.

CONCLUSIONS

Interaction (non-next-nearest neighbor) terms accounting for steric or electronic effects have been developed for $\Delta_f H^{\ominus}$, $S^{\ominus}$ and $C_p(T)$ for multiple Br, Cl, F, CH_3 and OH substituents on aromatic compounds. Comparisons of group additivity with these interactions to Benson group estimates and to literature values, show that the use of interaction terms improves the accuracy of the estimation method. The entropy and heat capacity group data allow calculation of ΔG and equilibrium constants for reactions of these species over any desired range of temperature when combined with the harmonic oscillator–heat capacity extrapolation in THERM.

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Copies of this group interaction data file and THERM are available free on disk by writing to the authors.

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