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Group additivity values for enthalpies of formation (298 K), entropies (298 K), and molar heat capacities (300 K < T < 1500 K) of gaseous fluorocarbons

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Received 22 November 2006; received in revised form 20 March 2007; accepted 21 March 2007

Available online 5 April 2007

Abstract

A group additivity method was developed to estimate standard enthalpies of formation and standard entropies at 298 K of linear radical and closed-shell, gaseous fluorocarbon neutrals containing four or more carbon atoms. The method can also be used to estimate constant pressure molar heat capacities of the same compounds over the temperature range 300 K to 1500 K. Seventeen groups and seven fluorine–fluorine interaction terms were defined from 12 fluorocarbon molecules. Interaction term values from Yamada and Bozzelli [T. Yamada, J.W. Bozzelli, J. Phys. Chem. A 103 (1999) 7373–7379] were utilized. The enthalpy of formation group values were derived from G3MP2 calculations by Bauschlicher and Ricca [C.W. Bauschlicher, A. Ricca, J. Phys. Chem. A 104 (2000) 4581–4585]. Standard entropy and molar heat capacity group values were estimated from *ab initio* geometry optimization and frequency calculations at the Hartree–Fock level using the 6-31G(d) basis set. Enthalpies of formation for larger fluorocarbons estimated from the group additivity method compare well to enthalpies of formation found in the literature.

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Keywords: Enthalpy of formation; Entropy; Molar heat capacity; Radicals

1. Introduction

Gaseous fluorocarbons are commonly used in chemical vapor deposition (CVD) of fluorocarbon thin films. Disagreement exists as to whether films are deposited *via* heterogeneous polymerization reactions, whereby growth occurs *via* the reactions of monomers at the surface of a growing film, or through homogeneous polymerization reactions, whereby films accumulate by the deposition of high molecular weight species that are formed through gas-phase chemistry [1]. In the latter case, large radical species would primarily contribute to film growth, due to their high reactivity. Similarly, it is proposed that large fluorocarbon radicals polymerize in the gas phase, leading to

powder formation in low-pressure fluorocarbon plasmas commonly used in the microelectronics industry [2,3]. Knowledge of thermodynamic properties of large fluorocarbon molecules and short-lived species, such as radicals, is important for an understanding of these complex chemical processes.

Thermodynamic data for large fluorocarbon molecules, especially radicals, are limited. Experimental thermodynamic data are available for only a few fluorocarbon species containing more than two carbon atoms. Enthalpy of formation values are reported in the literature for several closed shell compounds, including C₃F₆ [4,5], C₃F₈ [6], *n*-C₄F₈ [7], C₄F₁₀ [7,8], C₆F₁₂ [9], C₇F₁₆ [6], C₉F₁₈ [9], and C₁₀F₂₂ [10]. Limited data for fluorocarbon radicals are available in Orlov *et al.* [11]. More extensive work has been done by means of *ab initio* computational studies, including a study by Zachariah *et al.* [12] that reported

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thermochemical data for C_1 and C_2 hydrofluorocarbon species. Bauschlicher and Ricca [13] performed a more comprehensive *ab initio* study, and reported enthalpies of formation for fluorocarbon molecules, including radicals, containing up to three carbon atoms. Stewart also conducted an extensive semiempirical study that reports enthalpies of formation for select fluorocarbon molecules such as C_4F_6 , n - C_4F_8 , and C_4F_{10} [14]. Computational chemistry calculations become more expensive as the size and complexity of the molecule grows, making studies of this sort impractical at present for exploration of large fluorocarbon molecules.

Group additivity methods have been successfully used to determine thermodynamic properties for systems where neither thermodynamic data nor accurate estimation methods are available. The concept of group additivity has been successfully applied to hydrocarbon [15], partially halogenated hydrocarbon [16], and silicon hydride systems [17]. In general, group additivity allows for estimation of a molecule's thermodynamic properties by summing the property values of contributing groups, *i.e.*, “group additivity values” (GAVs). However, fluorocarbons are not a good candidate for the traditional group additivity method as defined by Benson [15,16], which does not fully account for the steric or electrostatic interactions between fluorine atoms on adjacent carbon atoms. Yamada and Bozzelli [18] reported average errors when using the traditional Benson group additivity that exceeded $40 \text{ kJ} \cdot \text{mol}^{-1}$, but noted that these errors were dramatically reduced by using a modified group additivity method, one that corrects for fluorine–fluorine interactions.

Yamada and Bozzelli [18,19] and Zhang and Pollard [20] derived group additivity values for two partially fluorinated systems, hydrofluorocarbons and chlorofluorocarbons. While nothing prevents applying these GAVs to fully fluorinated systems, they could not be applied to most radical systems. Yamada and Bozzelli reported no radical group GAVs, while Zhang and Pollard reported GAVs for two radical groups. This makes it impossible to study the gas-phase chemistries discussed above, where one expects large numbers of short-lived radicals. In this paper, we report group additivity values, including corrections for fluorine–fluorine interactions, which can be used to estimate standard enthalpies of formation $\Delta_f H^\circ$, standard entropies S° , and molar heat capacities $C_p^\circ(T)$ for linear radical and closed-shell gaseous fluorocarbon neutrals containing four or more carbon atoms.

2. Methods

The challenge in devising a “good” group additivity method is to identify a set of groups that is large enough to provide reasonable predictions and yet small enough that it can be derived from an existing data set. Therefore, the validity of any set of GAVs depends on the precision of the input data and on the size of the database. Bauschlicher and Ricca [13] calculated enthalpies of forma-

tion of C_xF_y ($x = 1$ to 3) at the G3MP2 [21] level of theory, with estimated errors of $\pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$. We chose to base our $\Delta_f H^\circ$ group additivity analysis on these values because there is no experimental study, to our knowledge, that could provide us with as large or as accurate a database. We used data for two singly-bonded molecules (C_2F_6 and C_3F_8), three singly-bonded radicals (C_2F_5 , 1 - n - C_3F_7 , and 2 - n - C_3F_7), three doubly-bonded molecules (C_2F_4 , C_3F_4 , and C_3F_6), three doubly-bonded radicals (C_2F_3 , C_3F_2 , and C_3F_3), and one triply-bonded molecule (C_2F_2). For these same molecules, we performed an *ab initio* geometry optimization and frequency calculation at the Hartree–Fock level using the 6-31G(d) basis set to determine entropies and molar heat capacities. This calculation was carried out using Gaussian-03 [22]. The vibrational frequencies were scaled by the standard factor of 0.8929, and S° and $C_p^\circ(T)$ were subsequently calculated using a rigid-rotor/harmonic-oscillator approximation. The enthalpies of formation from the Bauschlicher and Ricca study, along with our calculated entropy and molar heat capacities, are shown in table 1. From the available database of molecules, 17 groups and seven fluorine–fluorine interaction terms are defined, as illustrated in figure 1. Some groups and interaction terms are present in several molecules but are only defined once in figure 1 for the sake of clarity.

This database of 12 molecules was not large enough to calculate group values and fluorine–fluorine interaction terms. Therefore, we use interaction terms determined by Yamada and Bozzelli [18] based on G2MP2 [23] calculations performed on hydrofluorocarbons. These interaction terms are shown in table 2.

Given that consistent thermochemical data are available for only 12 molecules, while 17 groups are defined, five further assumptions are required to determine the set of GAVs. First, we assumed that $C\text{--}[F]_3[C]$ is equivalent to $C\text{--}[F]_3[C]$. The analog to this assumption in the hydrocarbon system, namely that $C\text{--}[H]_3[C]$ is equivalent to $C\text{--}[H]_3[C]$, is commonly made, and Marsi *et al.* [24] determined that on average it affects $\Delta_f H^\circ$ GAVs by only $2.1 \text{ kJ} \cdot \text{mol}^{-1}$ in an alkyl radical system. Therefore, we supposed that setting the GAVs for $C\text{--}[F]_3[C]$ equal to those of $C\text{--}[F]_3[C]$ would have only a small effect on the fluorocarbon results as well. Similarly, we assigned the GAV of $C_d\text{--}[F]_2[C]$ to be equal to that of $C_d\text{--}[F]_2[C]$. We also assumed that the GAVs of $C\text{--}[F]_3[C_d]$ were equal to that of $C\text{--}[F]_3[C]$, which was supported by Cohen and Benson [25] in the hydrocarbon system, for which they found that the GAVs of $C\text{--}[H]_3[C_d]$ equaled those of $C\text{--}[H]_3[C]$. Based on the same logic we further assumed that the GAVs of $C_d\text{--}[F][C_d]$ equaled those of $C_d\text{--}[F][C]$. Finally, we assigned the $\Delta_f H^\circ$ GAV of $[C]\text{--}C_n\text{--}[C]$ to be equal to Cohen and Benson's value [25] of $142.3 \text{ kJ} \cdot \text{mol}^{-1}$ for the same group. The S° and $C_p^\circ(T)$ GAVs were assigned Benson's values [16] also and can be seen in table 3.

From these assumptions, a step-by-step approach was used to derive group additivity values from the available

TABLE 1

Enthalpies of formation, $\Delta_f H^\circ$, from Bauschlicher and Ricca [13] and calculated entropy, S° , and molar heat capacities, $C_p(T)$, used in determination of group additivity values

Species	$\Delta_f H^\circ$ (298 K)/(kJ · mol ^{−1})	S° (298 K)/(J · mol · K ^{−1})	C_p (T)/(J · mol · K ^{−1})						
			300	400	500	600	800	1000	1500
Single bonded species									
C ₂ F ₅	−900.77	324.7	93.3	107.9	119.2	127.6	138.5	144.8	151.5
C ₂ F ₆	−1348.67	333.5	105.9	123.4	136.8	146.9	159.4	166.9	175.3
1- <i>n</i> -C ₃ F ₇	−1320.64	407.9	136.8	158.6	175.3	187.9	203.8	213.0	223.4
2- <i>n</i> -C ₃ F ₇	−1348.96	415.9	136.0	158.2	175.3	187.9	203.8	213.0	223.4
C ₃ F ₈	−1765.65	412.5	149.4	174.1	192.9	206.7	225.1	235.1	246.9
Double bonded species									
C ₂ F ₃	−224.14	300.4	68.2	76.6	83.3	88.3	95.0	98.7	103.8
C ₂ F ₄	−676.51	299.6	80.3	91.6	100.0	106.3	115.1	120.5	126.8
C ₃ F ₂	230.91	302.5	65.7	74.1	80.3	85.4	92.5	97.1	102.5
C ₃ F ₃	−133.64	331.0	84.9	95.0	102.5	108.4	116.7	121.3	127.2
C ₃ F ₄	−553.71	329.7	92.0	106.3	116.7	124.7	135.6	142.3	150.2
C ₃ F ₆	−1154.95	377.4	121.3	140.2	154.8	165.7	180.3	188.7	198.7
Triple bonded species									
C ₂ F ₂	0.13	246.0	59.0	64.4	68.2	71.1	75.3	78.2	82.4

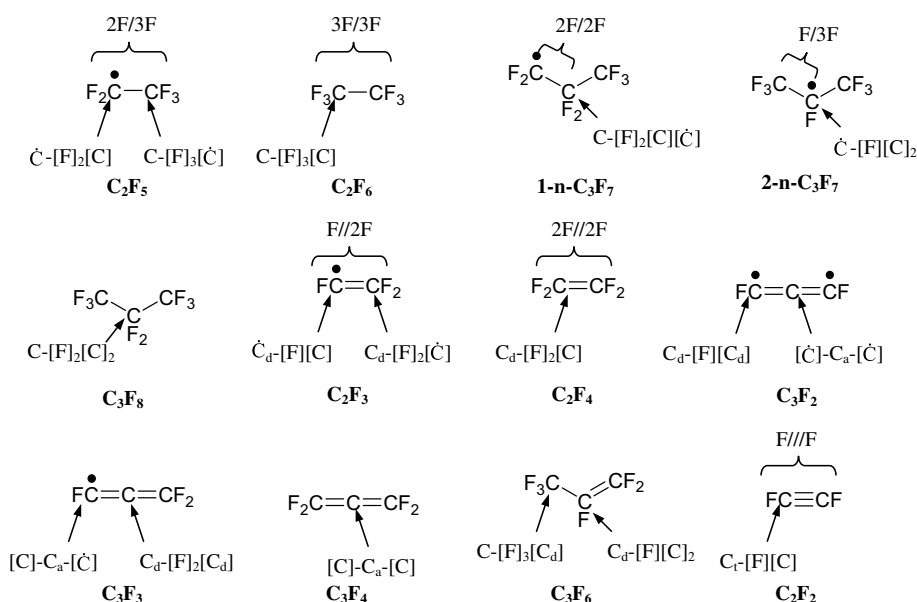


FIGURE 1. Definition of groups and fluorine–fluorine interaction terms from 12 fluorocarbon molecules. C[•]: carbon radical. C_d: double-bonded carbon. C_a: allyl-like carbon ([C] = C = [C]). C_t: triple-bonded carbon. /, //, /// indicate interaction across a single, double, and triple bond, respectively.

database. Though this is not as desirable as conducting a least-squares-fit over a large database of molecules, Cohen and Benson [25] found that GAVs determined from accurate data for single molecules were able to reproduce the thermodynamic properties of larger molecules within experimental uncertainty. Given the fluoro-carbon–fluorocarbon interaction values determined by Yamada and Bozzelli [18], GAVs for C-[F]₃[C], C_d-[F]₂[C], and C_t-[F][C] were determined directly from additivity applied to C₂F₆, C₂F₄, and C₂F₂, respectively. With these values, GAVs for C-[F]₂[C]₂ could be determined from C₃F₈. Next, GAVs for C[•]-[F]₂[C], C[•]-[F][C]₂, and C-[F]₂[C][C[•]] could be derived from

C₂F₅, 2-*n*-C₃F₇, and 1-*n*-C₃F₇, respectively, once the equivalence of C-[F]₃[C[•]] and C-[F]₃[C] was assumed. After C_d-[F]₂[C[•]] was assumed equivalent to C_d-[F]₂[C], GAVs for C[•]_d-[F][C] were found from C₂F₃. Then, based on the GAVs assigned to [C]-C_a-[C] and the assumed equivalence of C[•]_d-[F][C_d] to C[•]_d-[F][C], GAVs for C_d-[F]₂[C_d], [C]-C_a-[C[•]], and [C[•]]-C_a-[C[•]] were determined from C₃F₄, C₃F₃, and C₃F₂, respectively. Finally, from the equivalence of C-[F]₃[C_d] to C-[F]₃[C], GAVs for C_d-[F][C]₂ were found from C₃F₆. The results are listed in table 3, which gives GAVs for standard enthalpies of formation and entropies at 298 K, and molar heat capacities over the range 300 to 1500 K.

TABLE 2

GAV correction values for enthalpy of formation, $\Delta_f H^\circ$, entropy, S° , and molar heat capacities, $C_p(T)$, due to interactions between fluorine atoms on adjacent carbon atoms

Fluorine Correction Terms	$\Delta_f H^\circ(G_n, 298 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$	$S^\circ(G_n, 298 \text{ K})/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$C_p(G_n, T) (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$						
			300	400	500	600	800	1000	1500
F/2F	23.8	1.59	1.26	1.05	0.71	0.63	0.13	0.13	0.42
F/3F	32.6	3.56	−0.59	−0.84	−1.00	−0.88	−1.09	−0.88	−0.25
2F/2F	41.0	−1.88	6.74	5.06	3.22	2.01	0.38	0.04	0.25
2F/3F	57.7	3.05	0.33	−0.63	−1.26	−1.42	−1.72	−1.42	−0.54
3F/3F	64.9	2.26	1.00	−0.38	−1.17	−1.42	−1.63	−1.30	−0.54
F//F	7.9	−30.71	−0.04	−0.42	−0.50	−0.38	−0.13	0.13	0.42
F//2F	37.2	−15.48	2.31	0.63	−0.08	−0.29	−0.29	−0.13	0.21
2F//2F	67.4	−10.96	4.69	1.55	0.08	−0.46	−0.63	−0.42	0.00
F///F	−2.1	−21.63	−4.06	−3.01	−2.01	−1.21	−0.33	−0.08	−0.13

Values are from Yamada and Bozzelli [18].

TABLE 3

Group additivity values for enthalpy of formation, $\Delta_f H^\circ$, entropy, S° , and molar heat capacities, $C_p(T)$, for fluorocarbon molecules

Group	$\Delta_f H^\circ(G_n, 298 \text{ K})^a$		$S^\circ(G_n, 298 \text{ K})^b$		$C_p(G_n, T)^b$						
	This work	Reference [18]	This work	Reference [18]	300	400	500	600	800	1000	1500
C-[F] ₃ [C]	−706.8	−703.7	173.04	178.03	52.46	61.95	69.02	74.10	80.61	84.10	87.90
C-[F] ₃ [C] ^c	−706.8		173.04		52.46	61.95	69.02	74.10	80.61	84.10	87.90
C-[F] ₃ [C] _d ^c	−706.8		173.04		52.46	61.95	69.02	74.10	80.61	84.10	87.90
C-[F] ₂ [C] ₂	−467.6	−438.9	60.95	72.38	44.08	51.38	57.79	61.51	67.45	70.11	72.39
C-[F] ₂ [C][C] ^c	−460.9		67.36		36.89	45.53	52.94	58.07	65.03	68.33	71.49
C-[F] ₂ [C]	−251.8		166.86		40.87	46.78	51.83	55.00	59.72	62.03	64.29
C-[F][C] ₂	−0.7		63.08		32.70	36.10	39.61	41.30	45.04	46.70	48.14
C _d -[F] ₂ [C]	−371.9	−363.2	161.00	161.29	37.80	44.99	49.97	53.47	57.92	60.46	63.42
C _d -[F] ₂ [C] _d	−348.0		157.98		37.97	43.88	48.51	51.88	56.66	59.53	63.11
C _d -[F] ₂ [C] ^c	−371.9		161.00		37.80	44.99	49.97	53.47	57.92	60.46	63.42
C _d -[F][C] ₂	−146.1		55.83		29.76	33.63	37.34	39.43	43.32	45.30	47.35
C _d -[F][C]	110.6		155.10		28.31	30.93	33.38	34.95	37.36	38.63	40.02
C _d -[F][C] _d ^c	110.6		155.10		28.31	30.93	33.38	34.95	37.36	38.63	40.02
[C]-C _a -[C] ^c	142.3		25.10		16.32	18.41	19.66	20.92	22.18	23.01	23.85
[C]-C _a -[C] ^c	103.8		18.09		18.78	20.11	20.91	21.72	22.75	23.46	24.29
[C]-C _a -[C] ^c	9.8		−7.39		9.29	11.99	13.67	15.43	17.87	19.79	22.50
C _t -[F][C]	1.1	11.7	136.60	134.22	31.50	33.71	35.14	36.22	37.92	39.25	41.30

^a Units of $\text{kJ} \cdot \text{mol}^{-1}$.

^b Units of $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

^c Assumed value.

3. Results and discussion

Any direct comparison between our group additivity values and those from other studies is relevant only to the extent that the other studies also included fluorine–fluorine interaction corrections. Therefore, GAVs of this work can be compared only with those determined by Yamada and Bozzelli [18]. Comparison of the $\Delta_f H^\circ$ and S° GAVs of the four groups coincident in both studies, shown in table 3, resulted in an average difference of $12.8 \text{ kJ} \cdot \text{mol}^{-1}$ and $4.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. There are discrepancies in the enthalpy of formation GAVs of $28.7 \text{ kJ} \cdot \text{mol}^{-1}$ for group C-[F]₂[C]₂ and $10.6 \text{ kJ} \cdot \text{mol}^{-1}$ for group C_t-[F][C]. However, these differences must be considered in light of the entire group additivity scheme. Yamada and Bozzelli utilized a hydrofluorocarbon system, *i.e.*, an entirely different set of molecules, in determining their additivity values.

Discrepancies are therefore expected due to uncertainties within the molecule data set used in calculating the GAVs. As long as a consistent scheme is used for estimating thermodynamic properties, any “error” introduced by one group should be countered by the other GAVs used to calculate the thermodynamic value.

Thermodynamic properties determined using these group additivity values were also compared to experimental values. However, these comparisons are limited because few experimental enthalpies and no experimental entropies, to our knowledge, exist for fluorocarbons with four or more carbon atoms. Comparison was made for molecules where enthalpies could be found in the literature and are shown in table 4. Due to the lack of experimental data, evaluation was also made against one computational study by Stewart [14]. The enthalpies determined using our group additivity replicate the data from the literature well.

TABLE 4

Comparison of estimated enthalpies of formation, $\Delta_f H^\circ$, to those found in the literature

Molecule	$\Delta_f H^\circ$ (298 K)/(kJ · mol ⁻¹)	
	Experimental	Group additivity
C ₄ F ₆	−1060.0 ^a	−948.5
n-C ₄ F ₈	−1631.0 ^a , −1650.0 ^b	−1632.2
C ₄ F ₁₀	−2140.0 ^b , −2156.0 ^a , −2233.8 ^c	−2192.4
C ₇ F ₁₆	−3385.4 ± 3.6 ^d	−3472.7

^a Reference [14].

^b Reference [7].

^c Reference [8].

^d Reference [6].

Acknowledgements

This work was partially supported by NSF IGERT Grant DGE-0114372, by a NSF Graduate Research Fellowship, and by the Minnesota Supercomputing Institute.

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