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Thermochemical Properties of Halides and Halohydrides of Silicon and Carbon

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Atomization energies, enthalpies of formation, entropies as well as heat capacities of the SiH_nX_m and CH_nX_m systems, with X being F, Cl and Br, have been studied using quantum chemical calculations. The Gaussian-4 theory (G4) and Weizman-1 theory as modified by Barnes et al. 2009 (WIRO) have been applied in the calculations of the electronic, zero point and thermal energies. The effects of low-lying electronically excited states due to spin orbit coupling were included for all atoms and diatomic species by mean of the electronic partition functions derived from the experimental or computational energy splittings. The atomization energies, enthalpies of formation, entropies and heat capacities derived from both methods were observed to be reliable. The thermochemical properties in the temperature range of 298–2500 K are provided in the form of 7-coefficient NASA polynomials.

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Silicon carbide (SiC) is an attractive material for power electronics. The characteristics of having wide bandgap, high thermal conductivity, high blocking voltage and switching frequencies have made it superior for applications at high temperatures, frequencies and voltages.¹ To this end, it is vital to achieve high material quality as well as manufacturing process reliability and efficiency. In chemical vapor deposition (CVD), a widely used fabrication method for SiC layers, this means suppressing the formation of Si clusters and parasitic depositions which are known to introduce defects and degrade the growing layers, along with shortening the lifetime of reactor components.^{2–4} Halogenated gases have been utilized to reduce the cluster formation by breaking the Si-Si bonds in the clusters and forming the stronger Si-halogen bonds and consequently introduce a new parameter into the process, namely the halogen/Si ratio. This ratio has shown impacts on not only the cluster formation and parasitic growth, but also on the growth rates as well as defect formations.^{4,5}

In complex processes such as CVD, computational modeling has become essential in research as well as process development and design. Modeling accuracy and correctness depend crucially on the quality of the kinetics and thermochemistry data input. Thermochemistry data of some halides and halohydrides of Si and C are provided in databases,^{6–8} review,⁹ as well as experimental^{10–16} and theoretical studies.^{17–32} Nevertheless, inconsistency derived from various means of achieving data along with many data mismatches have rendered it far from complete. Here we present thermochemical properties from quantum chemical calculations of a complete set of halides and halohydrides of Si and C, namely SiX_nH_m and CX_nH_m with X = F, Cl and Br, and $n+m \leq 4$, covering the temperature range of 298–2500 K. The study range accommodates applications such as CVD process, surface etching of semiconductors, combustion, as well as fundamental studies. The quantum chemistry composite methods of Gaussian-4 theory (G4)³³ are utilized and compared to the Weizmann-1 theory^{34,35} as modified by Barnes et al. 2009³⁶ (WIRO).

Computational Methods

All quantum chemical calculations were carried out using Gaussian 09.³⁷ The G4 and WIRO methods are described in detail in Ref. 33 and Ref. 34–36. Both methods are designed to achieve the total energy from its additives derived from different levels of theories. The G4 uses the B3LYP/6-31G(2df,p) level in the geometry optimization as well as the harmonic frequency calculation. The frequencies are then scaled using a factor of 0.9854 – a factor optimized for the zero point energy (ZPE) calculated at this level. The electronic energy is composed of the following terms: the Hartree-Fock (HF)

limit energy, the electron correlation energy, the higher level empirical corrections (HLCs) and for atoms the spin-orbit corrections. The inclusion of HLCs significantly helps reducing the computational cost while maintaining the accuracy within acceptable range. The theory is attractive to applications on halide systems due to many improvements over its previous version, Gaussian-3 (G3),^{38,39} such as an addition of a complete basis set limit (CBS) extrapolation of the HF energy, the increase of the *d*-polarization sets on the first- and second-row atoms with the exponents reoptimized for the latter, and an improvement in the HLCs on radicals.

WIRO theory is based on the geometry optimized at the B3LYP/cc-pVTZ(+d) level, where (+d) refers to the addition of a tight *d* function in the presence of second-row atoms. The harmonic frequencies are obtained from the same level and scaled with a factor of 0.985 – also a scaling factor for ZPE. The electronic energy is composed of the CBS values of the self-consistent field energy (SCF), the coupled cluster with all single and double substitutions (CCSD) and its perturbative triple excitation correction (T) together with the core correlation and scalar relativistic energy following the method modified by Barnes et al.,³⁶ and the spin orbit corrections for atoms. Both close-shell and open-shell molecules are treated similarly using the spin-restricted theory, and henceforth referred to as WIRO following Barnes et al.³⁶ Apart from the spin orbit corrections and extrapolations, the WIRO contains no empirical corrections.

The electronic energy, ZPE and thermal energy at 298 K from scaled harmonic frequencies contribute to the energy at 0 K (H^0) and the enthalpies at 298 K (H^{298}). The atomization energies at 0 K (ΣD_0 (0 K)) and enthalpies of formation (ΔH_f°) at 0 K and 298 K are derived from the following equations,

$$\Sigma D_0(0\text{ K}) = \Sigma_{\text{atom}}[H^0]_{\text{atoms}} - H^0_{\text{molecule}}, \quad [1]$$

$$\Delta H_f^\circ(0\text{ K}) = \Sigma_{\text{atom}}[\Delta H_f^\circ(0\text{ K})]_{\text{atoms}} - \Sigma D_0(0\text{ K}), \quad [2]$$

$$\Delta H_f^\circ(298\text{ K}) = \Delta H_f^\circ(0\text{ K}) + (H^{298} - H^0)_{\text{molecule}} - \Sigma_{\text{atom}}[H^{298} - H^0]_{\text{atom}}. \quad [3]$$

The atomic $\Delta H_f^\circ(0\text{ K})$ and the atomic thermal enthalpy corrections at 298 K ($H^{298} - H^0$) used in the study are shown in Table I.

The $\Delta H_f^\circ(298\text{ K})$ and the thermal enthalpy corrections at temperature T ($H^T - H^{298}$) provide the absolute enthalpy, $\Delta H^T \equiv \Delta H_f^\circ(298\text{ K}) + [H^T - H^{298}]$. In contrast to ($H^{298} - H^0$) and ZPEs, vibrational contributions to ($H^T - H^{298}$), entropies (S^T) and heat capacities (C_p^T) were calculated based on the unscaled harmonic frequencies rather than the ZPE scaled harmonic frequencies. The G4 and WIRO calculated ΔH^T , S^T and C_p^T are fitted into 2 sets of 7-coefficient NASA

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Table I. Atomic ΔH_f° (0 K) and thermal corrections to enthalpy at 298 K ($H^{298} - H^0$) in $\text{kJ} \cdot \text{mol}^{-1}$.

	ΔH_f° (0 K)	$H^{298} - H^0$		ΔH_f° (0 K)	$H^{298} - H^0$
Si	446 ± 8^a	3.218^a	C	711.19 ± 0.46^a	1.051^a
	445.67 ± 8.00^b	$3.217^{b,c}$		711.19 ± 0.45^b	1.050^b
	448.32 ± 0.84^c			711.198 ± 0.45^c	1.054^c
	448.5 ± 0.8^d				
	452.3 ± 2^e				
H	216.035 ± 0.006^a	4.234^{a-c}	F	77.28 ± 0.30^a	4.413^{a-c}
	216.04 ± 0.01^b			77.27 ± 0.30^b	
	216.034 ± 0.001^c			77.274 ± 0.058^c	
Cl	119.621 ± 0.006^a	4.591^{a-c}	Br	117.92 ± 0.06^a	12.255^a
	119.63 ± 0.01^b			117.93 ± 0.12^b	$12.260^{b,c}$
	119.620 ± 0.002^c			117.915 ± 0.06^c	

^aNIST-JANAF Database, 1998⁶; ^bNIST-CCCBDB Database⁴⁰; ^cGoos-Burcat-Ruscic Thermochemical Database for Combustion⁷; ^dKarton and Martin, 2007⁴⁶; ^eOchterski et al., 1995.⁵¹

polynomials, corresponding to the temperature ranges of 298.15–1000 K and 1000–2500 K.

Results and Discussion

Atomization energies (ΣD_0).— The electronic energies and ZPEs calculated using the G4 and WIRO methods are provided in supplementary material. The atomization energies (ΣD_0 (0 K)) derived from the G4 and WIRO methods are presented in Table II in comparison to the databases/experiments and theoretical calculations from literature. In contrast to the G4 method, the WIRO has been designed only for atoms up to the second-row of the periodic system. Therefore this method is only used here for the F- and Cl-systems.

It is clear from Table II that the database/experimental atomization energies for many species are inconsistent. On the other hand, good agreement is observed between our calculations and those derived from highly accurate computational methods reported by Feller et al.,²⁶ Feller and Dixon,²⁸ Vasiliu et al.,²⁷ Karton et al.,³⁰ Tajti et al.,³¹ Grant and Dixon³² and Klopper et al.²⁹ It is apparent that large dis-

crepancies of ~ 15 – 40 kJ mol^{-1} exist between the theoretical and experimental results (NIST-JANAF⁶ and NIST-CCCBDB⁴⁰) of SiF, SiF₂, CHF, SiH₃F and CH₃F (NIST-CCCBDB only), accompanied by small to moderate discrepancies of ~ 7 – 12 kJ mol^{-1} for SiH (NIST-JANAF only), CF and CF₂. Naturally, such discrepancies are observed in the corresponding ΔH_f° as shown later in Tables III and IV. The data from the active thermochemical table database (ATcT),²⁰ on the other hand, are much more agreeable to the theory.

It is observed by comparing the WIRO energies to the more expensive model of W4 theory³⁰ that the deviations in CF₄ and CH₂F₂ are caused by the slow convergence in the CCSD and SCF energies with increased basis sets, while the deviations in SiF₄ and SiH₃F are due to the core-correlation and scalar relativistic energies. This points out the necessity to consider calculation methods from higher levels if the results with higher accuracies are required.

On the other hand, the G4 theory is observed to depend strongly on the HLCs, which contributes ~ 14 – 30 kJ mol^{-1} to the ΣD_0 and helps to reduce computational costs tremendously. Compared to the more expensive methods, the G4 performs very nicely despite its low cost.

Table II. Atomization energies (ΣD_0 (0 K)) in $\text{kJ} \cdot \text{mol}^{-1}$ derived from the G4 and WIRO methods in comparison to the databases and experiments from literature. Due to the method construction, the WIRO is applied only to the F- and Cl-systems.

	This work		Literature/Databases	
	G4	WIRO	Databases/Experiments	Theory
SiH	296.6	294.6	287.1 ± 8.4^a , 294.8^b	294.9 ± 0.8^e , 295.0 ± 1.7^h
SiF	589.7	587.7	545.2 ± 12.6^a , 550.0^b	585.3 ± 1.7^h
SiF ₂	1235.6	1236.7	1187.6 ± 12.6^a	1231.8 ± 2.1^h
SiF ₃	1674.9	1678.2	1760.1 ± 16.7^a	
SiF ₄	2364.0	2370.9	2364.5 ± 0.84^a , 2364.3^b	2367.8^j
SiHF	897.1	897.2		
SiH ₂ F	1131.9	1135.7		1136.2^l
SiH ₃ F	1519.5	1525.8	1538.5 ± 20.9^a	1521.6^j , 1525.9^l
SiHF ₂	1401.8	1405.7		
SiH ₂ F ₂	1798.8	1806.3	1814.9 ± 20.9^a	
SiHF ₃	2088.5	2096.2	2087.5 ± 20.9^a	
SiCl	422.3	421.1	369.4 ± 6.7^a , 425.0^b	969.0^l
SiCl ₂	853.7	855.6	854.0 ± 3.3^a , 848.1^b	1349.2^l
SiCl ₃	1125.7	1129.2	1194.1 ± 16.7^a	
SiCl ₄	1583.4	1588.6	1585.1 ± 1.3^a , 1584.3^b	1591.1^f
SiHCl	724.9	725.6		
SiH ₂ Cl	963.3	967.9		
SiH ₃ Cl	1341.2	1348.2	1346.5 ± 8^a	
SiHCl ₂	1044.4	1049.3		
SiH ₂ Cl ₂	1422.0	1430.5	1430.3 ± 12.6^a	1431.2^f
SiHCl ₃	1505.3	1513.2	1512.0 ± 4.2^a	1514.9^f
SiBr	357.6		323.1 ± 46^a	

Table II. (Continued.)

	This work		Literature/Databases	
	G4	WIRO	Databases/Experiments	Theory
SiBr ₂	717.1		719.7 ± 16.7 ^a	
SiBr ₃	926.2		978.9 ± 63 ^a	
SiBr ₄	1297.7		1303.2 ± 16.7 ^a	
SiHBr	659.7			
SiH ₂ Br	897.4			901.6 ^l
SiH ₃ Br	1271.9		1273.9 ± 17 ^a	1279.3 ^l
SiHBr ₂	911.0			
SiH ₂ Br ₂	1280.4		1282.3 ± 17 ^a	
SiHBr ₃	1290.7		1292.3 ± 17 ^a	
CH	339.2	335.0	336.54 ± 17.5 ^a , 334.7 ^b	334.7 ± 0.4 ^e , 334.70 ^k
CF	548.7	545.6	536.9 ± 8 ^a	545.5 ± 0.8 ^e , 545.50 ^k
CF ₂	1060.6	1061.3	1048.2 ± 6.3 ^a , 1050.3 ^b , 1059.1 ± 0.8 ^c	1060.1 ± 1.3 ^e , 1060.0 ⁱ
CF ₃	1412.0	1412.2	1410.6 ± 4.2 ^a , 1412.2 ^b	1409.0 ± 1.7 ^e
CF ₄	1947.8	1954.7	1947.5 ± 1.3 ^a , 1947.5 ^b , 1947.9 ± 0.6 ^c	1947.7 ^g , 1949.5 ⁱ , 1947.6 ^j
CHF	858.4	857.1	879.3 ± 29 ^a , 899.5 ^b	857.0 ⁱ
CH ₂ F	1249.2	1250.2	1251 ± 8 ^d	1245.2 ^g , 1246.7 ^l
CH ₃ F	1664.6	1667.7	1662.9 ± 33 ^a , 1683.5 ^b , 1665.1 ± 0.6 ^c	1664.8 ^g , 1663.4 ⁱ , 1663.9 ^j
CHF ₂	1324.4	1325.1		
CH ₂ F ₂	1741.4	1745.7	1740.8 ± 1.7 ^a , 1742.4 ^b , 1741.7 ± 0.8 ^c	1741.5 ± 1.3 ^e , 1741.0 ^g , 1741.5 ⁱ , 1739.4 ^j
CHF ₃	1848.6	1854.5	1849.2 ± 3.3 ^a , 1848.8 ^b , 1848.7 ± 0.9 ^c	1849.2 ⁱ
CCl	403.0	398.5	332.5 ± 20 ^a , 395.0 ^b	
CCl ₂	724.2	719.7	713.1 ± 21 ^a , 721.6 ^b	
CCl ₃	1001.7	996.2	990.0 ± 8 ^a , 1000.2 ^b	
CCl ₄	1286.4	1278.4	1283.5 ± 2.1 ^a , 1283.1 ^b	1285.3 ^g
CHCl	728.8	726.2	712.8 ± 42 ^a	
CH ₂ Cl	1146.9	1146.6	1139 ± 4 ^d	1144.7 ^g , 1145.2 ^l
CH ₃ Cl	1552.6	1555.9	1554.7 ± 2.1 ^a , 1552.9 ^b	1553.7 ± 1.7 ^e , 1557.3 ^g
CHCl ₂	1076.4	1075.3		
CH ₂ Cl ₂	1468.7	1471.3	1471.2 ± 1.3 ^a , 1470.7 ^b	1467.5 ± 2.1 ^e , 1469.8 ^g
CHCl ₃	1382.3	1381.5	1384.4 ± 1.3 ^a , 1384.1 ^b	
CBr	330.7		314.8 ± 63 ^a	
CBr ₂	595.3			
CBr ₃	825.4			
CBr ₄	1050.1		1103 ^a , 1032.9 ^b	
CHBr	664.8			
CH ₂ Br	1085.4			1080.0 ^l
CH ₃ Br	1497.0		1498.2 ^b , 1496 ± 1 ^d	1498.7 ^g
CHBr ₂	955.9			
CH ₂ Br ₂	1353.2		1348.1 ^b	
CHBr ₃	1205.9			

^aBased on ΔH_f° (0 K) from NIST-JANAF database, 1998⁶; ^bNIST-CCCBDB database (experiment)⁴⁰; ^cActive thermochemical table database (ATcT)²⁹;

^dFeller et al., 2003 (experiment)⁵²; ^eFeller et al. 2008 (theory)²⁶; ^fVasiliiu et al. 2012 (theory)²⁷; ^gFeller et al. 2003 (theory)⁵²; ^hFeller and Dixon, 1999 (theory)²⁸; ⁱKlopper et al. 2009 (theory)²⁹; ^jKarton et al. 2011 (W4 theory)³⁰; ^kTajti et al. (theory)³¹; ^lGrant and Dixon 2009 (theory).³²

The method however produces small systematic deviations ($\sim 5\text{--}10$ kJ mol⁻¹) in the Si-Cl-H compounds, which are possibly caused by slow convergence of the correlation energies despite the increased *d* polarization sets, as previously observed by Curtiss et al.³³ It also should be noted that unlike the more expensive calculation procedures such as WIRO, Feller-Peterson-Dixon⁴⁵ etc., G4 do not explicitly include scalar relativistic calculations. It is possible that this omission may not be remedied sufficiently by the HLCs and may affect the accuracy in Br containing compounds.

Enthalpies of formation (ΔH_f°) at 0 and 298 K.— Tables III and IV present ΔH_f° at 0 and 298 K calculated from the G4 and WIRO ΣD_0 in comparison to the databases and literature. The G4 and WIRO ΔH_f° utilized the atomic properties respectively from the NIST-CCCBDB, and the NIST-CC-KM – the latter represents the NIST-CCCBDB with its atomic Si ΔH_f° (0 K) replaced by the recommended value from Karton and Martin, 2007.⁴⁶ Such matchings are suggested by the lowest deviations comparing to the literature.

The discrepancies observed in the case of diatomic molecules are partly due to the fact that the low-lying electronically excited states of the molecules resulted from spin orbit coupling (SOC) effects need to be taken into account when dealing with the temperature above 0 K. The inclusion of SOC effects are shown within parentheses in Table IV. The low lying excited states were taken into account in the electronic partition function using the following experimental energy splittings (in cm⁻¹): 142.830 for SiH⁴¹; 161.88 for SiF⁴¹; 207.21 for SiCl⁴¹; 418.0 for SiBr⁴¹; 27.950 for CH⁴¹; 77.1 for CF⁴¹; 466 for CBr⁴² and a calculated value of 136.9 for CCl.⁴³ The effects increase the enthalpies (in kJ mol⁻¹) by 0.57 for SiH; 0.61 for SiF; 0.67 for SiCl; 0.59 for SiBr; 0.16 for CH; 0.38 for CF; 0.56 for CCl and 0.53 for CBr. Despite the small effects for the enthalpies, the inclusion of SOC significantly improves the agreement between the experimental data and the calculated S^{298} and C_p^{298} , as shown later in Table V. The experimental and theoretical data of SOC corrections for more complex molecules are however scarce and it is beyond the scope of this study to calculate and include such effects further. The reader is referred to Ref. 44 for details of the SOC calculations.

Naturally due to their relation to ΣD_0 , we observed similar deviations in ΔH_f° in the set of species discussed previously in the last section, namely the deviation between the databases (NIST-JANAF and NIST-CCCBDB) ΔH_f° and the theoretical results reported in the literature and our calculations. Table IV also includes the calcula-

tion results from the ccCA methods^{47–49} for Si-F-H and Si-Cl-H¹⁷ for further comparison. As reported by DeYonker et al.,⁴⁸ the ccCA should give accuracy comparable to the G3X model⁵⁰ and thus is expected to be less accurate than the G4 and WIRO. Nevertheless, good agreement are observed overall between our calculations and

Table III. Enthalpies of formation (ΔH_f°) at 0 K in $\text{kJ} \cdot \text{mol}^{-1}$ derived from the G4 (with NIST-CCCBDB atomic properties) and WIRO (with NIST-CC-KM atomic properties) in comparison to literature. Due to the method construction, the WIRO is applied only to the F- and Cl-systems.

	This work		Literature	
	G4	WIRO	Databases/Experiments	Theory
SiH	365.2	369.9	374.89 ± 8.4 ^a , 366.9 ^b	
SiF	-66.8	-61.9	-21.91 ± 12.6 ^a , -27.06 ± 11 ^b , -49 ± 9 ^c	
SiF ₂	-635.4	-633.6	-587.01 ± 12.6 ^a , -637 ± 6 ^c	-634.7 ^j
SiF ₃	-997.4	-997.9	-1082.27 ± 16.7 ^a , -994 ± 5 ^c	
SiF ₄	-1609.2	-1613.3	-1609.43 ± 0.84 ^a , -1609.49 ± 0.8 ^b	-1615.9 ^j
SiHF	-158.1	-155.4		
SiH ₂ F	-176.9	-177.9		-177.4 ^m
SiH ₃ F	-348.5	-351.9	-367.16 ± 20.9 ^a	-350.6 ^m
SiHF ₂	-585.6	-586.6		
SiH ₂ F ₂	-766.5	-771.2	-782.25 ± 20.9 ^a	
SiHF ₃	-1195.0	-1199.8	-1193.66 ± 20.9 ^a	
SiCl	143.0	147.0	196.25 ± 6.7 ^a , 140.29 ± 41 ^b	
SiCl ₂	-168.8	-167.8	-168.74 ± 3.3 ^a , -163.2 ± 4.2 ^b	-168.6 ^j
SiCl ₃	-321.2	-321.8	-389.25 ± 16.7 ^a , -320 ± 8 ^c	
SiCl ₄	-659.2	-661.6	-660.57 ± 1.3 ^a , -660.08 ± 0.80 ^b	-664.0 ^j , -663.2 ^k
SiHCl	56.4	58.5	56.322 ^d	
SiH ₂ Cl	34.1	32.3		31.8 ^m
SiH ₃ Cl	-127.7	-132.0	-132.77 ± 8 ^a	-132.2 ^m
SiHCl ₂	-143.5	-145.5		
SiH ₂ Cl ₂	-305.0	-310.6	-313 ± 12.6 ^a	-310.5 ^k
SiHCl ₃	-484.7	-489.8	-491.15 ± 4.2 ^a , -489.6 ± 2.3 ^c	-490.8 ^k
SiBr	206.0		240.8 ± 46 ^a	
SiBr ₂	-35.5		-37.9 ± 16.7 ^a	
SiBr ₃	-126.8		-179.1 ± 63 ^a	
SiBr ₄	-380.3		-385.55 ± 16.7 ^a	
SiHBr	119.9			
SiH ₂ Br	98.3			97.5 ^m
SiH ₃ Br	-60.2		-61.84 ± 17 ^a	-64.0 ^m
SiHBr ₂	-13.4			
SiH ₂ Br ₂	-166.8		-168.4 ± 17 ^a	
SiHBr ₃	-275.2		-276.5 ± 17 ^a	
CH	588.1	592.3	590.683 ± 17.5 ^a , 592.5 ^b , 592.96 ± 0.25 ^e	593.12 ⁱ
CF	239.7	242.9	251.6 ± 8 ^a ,	243.3 ± 0.8 ^h , 243.50 ⁱ
CF ₂	-194.9	-195.5	-182.48 ± 6.3 ^a , -184.6 ± 8.4 ^b , -191.7 ± 1.4 ^e	-193.6 ± 1.2 ^h , -192.5 ^j
CF ₃	-469.0	-469.2	-467.52 ± 4.2 ^a , -469.19 ± 5 ^b , -462.7 ± 2 ^f	-464.8 ± 1.6 ^h
CF ₄	-927.5	-934.4	-927.23 ± 1.3 ^a , -927.23 ± 0.75 ^b , -927.2 ± 0.5 ^c	-927.8 ± 2.0 ^h , -930.9 ^j
CHF	146.1	147.4	125.2 ± 29 ^a , 105 ± 25 ^b	148.9 ± 1.2 ^h
CH ₂ F	-28.7	-29.6		-27.9 ± 1.6 ^h , -26.4 ^m
CH ₃ F	-228.1	-231.1	-226.3 ± 33 ^a , -246.97 ± 15 ^b , -231.5 ± 2.7 ^c	-228.5 ± 2.0 ^h , -228.1 ± 1.7 ⁱ
CHF ₂	-242.7	-243.3		-239.4 ± 2.6 ^h
CH ₂ F ₂	-443.6	-447.9	-443.01 ± 1.7 ^a , -444.55 ± 1.7 ^b	-442.6 ± 2.0 ^h
CHF ₃	-689.5	-695.5	-690.1 ± 3.3 ^a , -689.74 ± 2.3 ^b , -685.8 ± 2 ^f	-687.7 ± 2.0 ^h , -690.4 ± 2.1 ⁱ
CCl	427.8	432.3	498.3 ± 20 ^a , 435.81 ± 40 ^b	430.0 ± 1.1 ^h
CCl ₂	226.2	230.7	237.3 ± 21 ^a , 228.9 ± 8.4 ^b	229.0 ± 1.9 ^h , 231.0 ^j
CCl ₃	68.3	73.9	80.1 ± 8 ^a , 69.9 ± 2.5 ^b	73.7 ± 4.9 ^h
CCl ₄	-96.7	-88.8	-93.81 ± 2.1 ^a , -93.35 ± 1 ^b , -93.20 ± 0.55 ^e	-88.7 ± 6.4 ^h , -89.5 ^j
CHCl	318.0	320.7	334 ± 42 ^a	320.1 ± 2.3 ^h
CH ₂ Cl	116.0	116.3		119.4 ± 2.7 ^h , 117.6 ^m
CH ₃ Cl	-73.6	-76.9	-75.75 ± 2.1 ^a , -73.94 ± 0.6 ^b , -74.7 ± 0.35 ^c	-74.3 ± 3.1 ^h
CHCl ₂	90.1	91.2		91.2 ± 4.8 ^h
CH ₂ Cl ₂	-86.2	-88.8	-88.66 ± 1.3 ^a , -88.15 ± 0.3 ^b , -88.55 ± 0.74 ^e	-86.5 ± 4.2 ^h
CHCl ₃	-96.2	-95.4	-98.27 ± 1.3 ^a , -97.95 ± 1.1 ^b , -98.4 ± 0.8 ^c , -98.4 ± 1.1 ^g	-94.6 ± 5.3 ^h
CBr	498.4		514.3 ± 63 ^a	
CBr ₂	351.8		356.89 ^a	
CBr ₃	239.6			
CBr ₄	132.8		79.89 ^a , 150 ± 15 ^b	

Table III. (Continued.)

	This work		Literature	
	G4	WIRO	Databases/Experiments	Theory
CHBr	380.4			
CH ₂ Br	175.8			181.2 ^m
CH ₃ Br	-19.8		-21 ± 0.5 ^b	
CHBr ₂	207.1			
CH ₂ Br ₂	26.0		31 ± 15 ^b	
CHBr ₃	75.1		81.0 ± 4.9 ^g	

^aNIST-JANAF database⁶; ^bNIST-CCCBDB database (experiments)⁴⁰; ^cShuman et al., 2009 (experiments)¹³; ^dDeng et al., 2008 (experiments)⁵³; ^eATcT database²⁰; ^fRuscic et al., 1998 (evaluation)⁵⁴; ^gShuman et al., 2008 (experiments)¹²; ^hCsontos et al. 2010 (theory)²⁰; ⁱTajti et al. 2004 (theory)³¹; ^jThanthiriwattte et al. 2015 (theory)⁵⁵; ^kVasiliiu et al. 2012 (theory)²⁷; ^lFeller et al. 2012 (theory)⁵⁶; ^mGrant and Dixon 2009 (theory).³²

Table IV. Enthalpies of formation (ΔH_f°) at 298 K in $\text{kJ} \cdot \text{mol}^{-1}$ derived from the G4 (with NIST-CCCBDB atomic properties) and WIRO (with NIST-CC-KM atomic properties) in comparison to literature. Due to the method construction, the WIRO is applied only to the F- and Cl-systems. The parentheses present the result when the effects of low lying excited states due to spin orbit coupling (SOC) are included.

	This work		Literature	
	G4	WIRO	Databases/Experiments	Theory
SiH	366.4 (366.9)	371.2 (371.7)	376.66 ± 8.4 ^a , 368.64 ^b , 361.0 ^d	371.9 ^{aa}
SiF	-65.6 (-65.0)	-60.7 (-60.1)	-20.083 ± 12.6 ^a , -25.23 ± 11 ^b , -47 ± 9 ^c , 7.1 ^d , -21 ± 25 ^e	-58.2 ^{aa}
SiF ₂	-636.2	-634.4	-587.852 ± 12.6 ^a , -638 ± 6 ^c , -619.0 ^d , -590 ± 8 ^e , -595.8 ± 7 ^f	-635.5 ^y , -631.1 ^{aa}
SiF ₃	-1000.4	-1000.8	-1085.33 ± 16.7 ^a , -998 ± 4.6 ^c , -1000 ± 21 ^e , -1075 ± 11 ^f	-988.1 ^{aa}
SiF ₄	-1614.6	-1618.6	-1614.94 ± 0.84 ^a , -1615.0 ± 0.8 ^b , -1615.78 ± 0.5 ^g	-1621.3 ^y , -1610.4 ^z , -1605.9 ^{aa}
SiHF	-159.7	-157.0		-156.2 ^{aa}
SiH ₂ F	-182.3	-183.2		-177.1 ^{aa}
SiH ₃ F	-357.8	-361.3	-376.56 ± 20.9 ^a , -415.9 ± 8 ^h	-357.2 ^{aa}
SiHF ₂	-590.1	-591.0		-582.0 ^{aa}
SiH ₂ F ₂	-775.0	-779.6	-790.776 ± 20.9 ^a , -804.2 ± 8 ^h	-772.9 ^{aa}
SiHF ₃	-1202.0	-1206.8	-1200.808 ± 20.9 ^a , -1225.9 ± 8 ^h	-1197.3 ^{aa}
SiCl	144.5 (145.2)	148.5 (149.2)	198.32 ± 6.7 ^a , 142.36 ± 41 ^b , 189.9 ^d , 155 ± 42 ^e , 154.8 ± 4 ⁱ	153.0 ^{aa}
SiCl ₂	-168.5	-167.6	-168.62 ± 3.3 ^{a,e} , -163.07 ± 4.2 ^b , -151 ± 8 ⁱ , -159 ± 6 ⁱ	-168.2 ^y , -161.3 ^{aa}
SiCl ₃	-321.9	-322.6	-390.37 ± 16.7 ^a , -334.7 ± 8 ^e , -318 ± 4 ⁱ , -321 ± 8 ^j , -326 ± 12 ^j	-307.3 ^{aa}
SiCl ₄	-661.0	-663.4	-662.75 ± 1.3 ^a , -662.2 ± 0.8 ^b , -657.0 ^d	-666.1 ^y , -665.3 ^z , 648.0 ^{aa}
SiHCl	55.1	57.2	54.945 ^k	59.9 ^{aa}
SiH ₂ Cl	29.1	27.2		34.9 ^{aa}
SiH ₃ Cl	-136.7	-140.9	-141.84 ± 8 ^a , -135.6 ± 10.5 ^e	-141.4 ^z , -135.5 ^{aa}
SiHCl ₂	-146.9	-148.9		-137.3 ^{aa}
SiH ₂ Cl ₂	-312.3	-317.9	-320.49 ^a , -315.1 ± 8.4 ^e	-318.0 ^z , -308.9 ^{aa}
SiHCl ₃	-489.5	-494.6	-496.22 ± 4.2 ^a , -513.00 ^d , -494.4 ± 2.3 ^j , -499.2 ± 7 ^j	-495.8 ^z , -482.3 ^{aa}
SiBr	200.0 (200.6)		235.3 ± 46 ^a , 209.0 ^d , 197 ± 42 ^e , 204 ± 8 ⁱ	
SiBr ₂	-49.8		-52.3 ± 16.7 ^a , -46 ± 8.4 ^e , -46 ± 4 ⁱ	
SiBr ₃	-148.8		-201.7 ± 63 ^a , -159 ± 8 ⁱ , -159 ± 25 ^e	
SiBr ₄	-410.0		-415.47 ± 16.7 ^a , -415.5 ^d , -416 ± 5 ⁱ , -415.5 ± 8 ^e	
SiHBr	111.2		-464.4 ^d	
SiH ₂ Br	85.9			
SiH ₃ Br	-76.5		-78.24 ± 17 ^a , -64.0 ± 9 ^e	
SiHBr ₂	-31.3			
SiH ₂ Br ₂	-188.6		-190.4 ± 17 ^a , -180.8 ± 10 ^e	
SiHBr ₃	-301.3		-302.9 ± 17 ^a , -317.6 ^d , -303.3 ± 9 ^e	
CH	591.4 (591.6)	595.7 (595.8)	594.128 ± 17.5 ^a , 594.13 ^b	596.2 ± 0.4 ^{ad}
CF	243.0 (243.4)	246.1 (246.5)	255.2 ± 8 ^a , 246.9 ± 0.7 ^l	247.0 ± 0.8 ^x , 246.4 ± 0.8 ^{ad}
CF ₂	-194.4	-195.0	-182.0 ± 6.3 ^a , -184.1 ± 8.4 ^b , -172 ± 8.4 ^m , -191.3 ± 1.4 ^l , -205 ± 13 ⁿ , -171.1 ± 10 ⁿ	-193.2 ± 1.2 ^x , -192.0 ^y , -194.1 ± 1.3 ^{ad}
CF ₃	-471.7	-471.9	-470.28 ± 4.2 ^a , -472 ± 5 ^b , -477.0 ^d , -429. ± 13 ^m , -465.7 ± 2 ^o , -467.4 ± 2.0 ^l	-467.6 ± 1.6 ^x , -469.0 ± 1.7 ^{ad}
CF ₄	-933.4	-940.2	-933.2 ± 1.3 ^a , -933.2 ± 0.75 ^b , -933.6 ^d , -930 ± 20 ^m , -933.4 ± 0.5 ^l	-933.8 ± 2.0 ^x , -936.8 ^y , -933.0 ^{ac}
CHF	146.4	147.7	125.2 ± 29 ^a , 105.29 ± 25 ^b , 109 ± 13 ⁿ , 156.9 ± 18 ⁿ , 143.1 ± 13 ⁿ	149.0 ± 1.2 ^x

Table IV. (Continued.)

	This work		Literature	
	G4	WIRO	Databases/Experiments	Theory
CH ₂ F	-32.1	-32.9	-32 ± 8.4 ^p , -34 ± 8 ^q	-31.2 ± 1.6 ^x , -28.0 ^{ac}
CH ₃ F	-236.1	-239.1	-236.577 ± 0.3 ^a , -255 ± 15 ^b , -247 ^m , -239.6 ± 2.7 ^l , -234 ± 4 ^q	-236.9 ± 2.0 ^x , -236.4 ^{ac} , -236.1 ± 1.7 ^{ab,ad}
CHF ₂	-246.1	-246.7	-239 ± 4.2 ^p	-243.0 ± 3.6 ^x
CH ₂ F ₂	-451.3	-455.5	-450.659 ± 1.7 ^a , -452.2 ± 1.7 ^b , -452.3 ^d , -452.21 ± 0.92 ^m	-450.5 ± 2.0 ^x , -450.6 ^{ac}
CHF ₃	-696.5	-702.3	-697.05 ± 3.3 ^a , -696.7 ± 2.3 ^b , -690.8 ^m , -695.4 ± 2.7 ^m , -695.3 ± 2.0 ^l , -692.9 ± 2 ^o	-694.9 ± 2.0 ^x , -697.3 ± 2.1 ^{ab,ad}
CCl	431.0 (431.6)	435.5 (436.1)	502.1 ± 20 ^a , 439.57 ± 40 ^b	433.7 ± 1.1 ^x
CCl ₂	227.5	232.0	238.5 ± 21 ^a , 221.8 ± 11 ^r , 230.1 ± 8 ⁿ , 163 ± 13 ⁿ , 239.3 ± 17 ⁿ , 213.4 ± 8 ⁿ , 218.0 ± 14 ⁿ	230.1 ± 1.9 ^x , 232.2 ^y
CCl ₃	67.9	73.4	79.5 ± 8 ^a , 71.1 ± 2.5 ^b , 59.0 ^d , 75.3 ± 8 ^s	73.1 ± 4.9 ^x
CCl ₄	-98.6	-90.7	-95.98 ± 2.1 ^a , -95.6 ± 1 ^b , -95.6 ± 2.5 ^m , -94 ± 2 ^m , -115 ± 3 ^m , -125 ± 4.6 ^m , -103 ± 7.9 ^m	-91.0 ± 6.4 ^x , -92.0 ^y , -93.3 ^{ac}
CHCl	318.3	321.0	335 ± 42 ^a , 312.1 ± 10 ^r , 326.4 ± 8 ⁿ , 297 ± 21 ⁿ , 316.7 ± 20.1 ⁿ , 336.4 ± 11 ⁿ	320.3 ± 2.3 ^x
CH ₂ Cl	114.2	113.8	121 ± 4 ^q , 117.3 ± 3.1 ^t , 115.9 ± 8 ^s	116.0 ± 2.7 ^x , 115.5 ^{ac}
CH ₃ Cl	-81.5	-84.8	-83.68 ± 2.1 ^a , -81.9 ± 1.5 ^m , -81.96 ± 0.67 ^m , -85.90 ± 0.59 ^m , -82.6 ± 0.4 ^l	-82.6 ± 3.1 ^x , -86.2 ^{ac}
CHCl ₂	87.8	89.0	80 ± 12 ^u , 89.0 ± 3.0 ^l , 93.3 ± 8 ^s	88.8 ± 5.8 ^x
CH ₂ Cl ₂	-93.0	-95.6	-95.521 ± 1.3 ^a , -95 ± 0.3 ^b , -95.1 ± 2.5 ^m , -95.7 ± 1.3 ^m , -95.4 ± 0.7 ^l	-93.7 ± 4.2 ^x , -93.7 ^{ac}
CHCl ₃	-100.9	-100.1	-103.18 ± 1.3 ^a , -102.7 ± 1.1 ^b , -102.9 ± 2.5 ^m , -103.3 ± 0.8 ^l	-99.7 ± 5.3 ^x
CBr	494.0 (494.6)		510.4 ± 63 ^a	
CBr ₂	338.5			
CBr ₃	217.9		235.0 ± 25 ^w , 205 ± 8 ^s	
CBr ₄	103.3		50.208 ^a , 120 ± 15 ^b , 83.9 ± 3.4 ^m	
CHBr	373.2			
CH ₂ Br	165.9		173.6 ^w , 169.0 ± 4 ^w , 168.2 ± 8 ^s	
CH ₃ Br	-35.2		-36.4 ± 0.5 ^b , -35.4 ^d , -38 ± 1.3 ^m , -34.3 ± 0.8 ^m , -37.5 ± 1.5 ^m	-36.8 ^{ac}
CHBr ₂	190.3		182 ± 20 ^u , 188.3 ± 8 ^w , 185.8 ± 8 ^s , 227.2 ^w	
CH ₂ Br ₂	4.6		10 ± 15 ^b , -11.1 ± 5 ^w	
CHBr ₃	49.2		55.4 ± 3.30 ^b , 23.8 ^d , 55.1 ± 4.9 ^v , 60.0 ± 15 ^w	

^aNIST-JANAF database⁶; ^bNIST-CCCBDB database (experiments)⁴⁰; ^cFisher et al., 1993 (experiments)¹⁵; ^dCRC database⁸; ^eWalsh, 1983 (evaluations)⁹; ^fWeber and Armentrout, 1988 (experiments)⁵⁷; ^gMartin and Taylor, 1999 (experiments)⁵⁸; ^hFarber and Srivastava, 1977 (experiments)⁵⁹; ⁱHildenbrand et al., 2003 (experiments)¹⁶; ^jShuman et al., 2009 (experiments)¹³; ^kDeng et al., 2008 (experiments)⁵³; ^lATcT database²⁰; ^mNIST Chemistry WebBook database (experiments)⁶⁰; ⁿPoutsma et al., 1997 (experiments)¹⁰; ^oRuscic et al., 1998 (evaluation)⁵⁴; ^pSchwartz et al., 2003 (experiments)²⁴; ^qFeller et al., 2003 (experiments)⁵²; ^rTian and Kass, 2007 (experiments)¹⁴; ^sHolmes and Lossing, 1988 (experiments)⁶¹; ^tSeetula 1996 (experiments)⁶²; ^uBorn et al., 2000 (experiments)¹¹; ^vShuman et al., 2008 (experiments)¹²; ^wPaddison and Tschuikow-Roux, 1998 (experiments)²³; ^xCsontos et al. 2010 (theory)²⁰; ^yThanthirivatte et al. 2015 (theory)⁵⁵; ^zVasiliiu et al. 2012 (theory)²⁷; ^{aa}Prascher et al. 2009 (theory)¹⁷; ^{ab}Feller et al. 2012 (theory)⁵⁶; ^{ac}Feller et al. 2003 (theory)⁵²; ^{ad}Feller et al. 2008 (theory).²⁶

Table V. Entropies (S) and heat capacities (C_p) at 298 K derived from the G4 and WIRO unscaled harmonic frequencies in comparison to the databases. Due to the method construction, the WIRO is applied only to the F- and Cl-systems. The parentheses present the result including the effects of low lying excited states due to spin orbit coupling (SOC).

Species	S ²⁹⁸ (J mol ⁻¹ · K ⁻¹)			C _p ²⁹⁸ (J mol ⁻¹ · K ⁻¹)		
	G4	WIRO	Literature	G4	WIRO	Literature
SiH	192.6 (197.8)	192.5 (197.8)	198.04 ^a , 198.05 ^b , 183.04 ^d	29.1 (30.0)	29.2 (30.1)	30.054 ^b , 29.171 ^d
SiF	220.5 (225.6)	220.6 (225.8)	225.7 ^a , 225.787 ^b , 225.8 ^c , 225.786 ± 0.17 ^d	31.4 (32.5)	31.6 (32.7)	32.65 ^d , 32.65 ^b , 32.6 ^c
SiF ₂	256.7	257.0	256.6 ^a , 256.58 ^b , 252.7 ^c , 256.579 ± 0.42 ^d	44.4	44.8	44.509 ^d , 43.9 ^c
SiF ₃	282.8	283.1	282.4 ^a , 282.381 ± 0.4 ^d	59.6	60.1	59.625 ^d
SiF ₄	283.2	283.8	282.76 ± 0.50 ^a , 282.75 ^a , 282.76 ± 0.50 ^b , 282.76 ± 0.50 ^c , 282.76 ± 0.42 ^d	73.7	74.3	73.621 ^d , 73.62 ^b , 73.6 ^c
SiHF	238.9	239.0		37.8	38.1	
SiH ₂ F	249.7	249.8		43.5	43.7	

Table V. (Continued.)

Species	S^{298} (J mol ⁻¹ · K ⁻¹)			C_p^{298} (J mol ⁻¹ · K ⁻¹)		
	G4	WIRO	Literature	G4	WIRO	Literature
SiH ₃ F	238.2	238.3	238.4 ^a , 238.402 ± 0.80 ^b , 238.4 ^c , 238.402 ± 0.8 ^d	47.0	47.2	47.196 ^d , 47.17 ^b , 47.4 ^c
SiHF ₂	271.9	272.1		50.5	50.8	
SiH ₂ F ₂	262.2	262.4	262.1 ^a , 262.130 ± 2.1 ^d	54.2	54.5	54.268 ^d
SiHF ₃	277.7	278.0	277.3 ^a , 271.9 ^c , 277.268 ± 0.8 ^d	63.6	64.0	63.485 ^d , 60.5 ^c
SiCl	233.0 (237.9)	233.0 (237.8)	237.81 ^a , 237.837 ± 0.21 ^b , 237.833 ± 0.21 ^d	34.2 (35.8)	34.2 (35.8)	35.78 ^d , 35.78 ^b , 36.9 ^c
SiCl ₂	282.4	282.4	281.3 ^a , 281.613 ^b , 281.333 ± 0.8 ^d	51.5	51.5	51.248 ^d , 51.27 ^b
SiCl ₃	321.0	320.9	318.13 ^a , 318.13 ^b , 318.189 ± 4.2 ^d	71.5	71.5	70.733 ^d
SiCl ₄	332.6	332.3	330.86 ^a , 331.446 ^b , 330.7 ^c , 330.945 ± 0.21 ^d	91.0	91.0	90.261 ^d , 90.4 ^b , 90.3 ^c
SiHCl	251.5	251.5		41.1	41.2	
SiH ₂ Cl	262.3	262.2		47.4	47.4	
SiH ₃ Cl	250.8	250.7	250.76 ^a , 250.761 ± 0.21 ^b , 250.7 ^c , 250.761 ± 0.21 ^d	51.2	51.2	51.098 ^d , 51.08 ^b , 51 ^c
SiHCl ₂	297.1	297.0		58.0	58.1	
SiH ₂ Cl ₂	287.2	287.1	286.72 ^a , 286.734 ± 0.34 ^b , 285.7 ^c , 286.734 ± 0.34 ^d	62.5	62.5	62.174 ^d , 62.17 ^b , 60.5 ^c
SiHCl ₃	314.9	314.7	313.71 ^a , 313.717 ± 0.40 ^b , 313.9 ^c , 313.717 ± 0.4 ^d	76.0	76.1	75.455 ^d , 75.44 ^b , 75.8 ^c
SiBr	244.6 (247.6)	-	247.51 ^a , 247.42 ± 0.21 ^d	35.2 (38.7)	-	38.731 ^d , 38.6 ^c
SiBr ₂	306.2	-	305.19 ^a , 305.22 ± 2.13 ^d	53.8	-	53.637 ^d ,
SiBr ₃	357.7	-	351.75 ^a , 351.77 ± 8.4 ^d	75.8	-	74.578 ^d ,
SiBr ₄	381.2	-	379.33 ^a , 377.9 ^c , 379.36 ± 0.8 ^d	97.5	-	97.009 ^d , 97.1 ^c
SiHBr	263.2	-		42.4	-	
SiH ₂ Br	274.1	-		49.0	-	
SiH ₃ Br	262.6	-	262.46 ^a , 262.4 ^c , 262.47 ± 0.21 ^d	53.0	-	52.865 ^d , 52.8 ^c
SiHBr ₂	321.1	-		61.1	-	
SiH ₂ Br ₂	311.0	-	310.0 ^a , 309.7 ^c , 310.05 ± 1.3 ^d	65.9	-	65.545 ^d , 65.5 ^c
SiHBr ₃	351.0	-	348.0 ^a , 348.6 ^c , 348.05 ± 0.4 ^d	81.0	-	80.41 ^d , 80.8 ^c
CH	177.1 (182.9)	177.0 (182.7)	183.04 ^{a-b-d}	29.1 (29.1)	29.1 (29.1)	29.175 ^b , 29.171 ^d
CF	207.2 (212.8)	207.3 (212.9)	213.03 ^a , 213.03 ± 0.04 ^b , 213.03 ± 0.04 ^d	29.6 (29.9)	29.7 (30.0)	30.06 ^d , 30.06 ^b
CF ₂	240.7	240.8	240.83 ^a , 240.838 ^b , 240.833 ± 0.04 ^d	38.6	38.9	38.948 ^d , 38.94 ^b
CF ₃	264.5	264.7	265.08 ^a , 264.562 ^b , 264.5 ^c , 265.082 ± 4.2 ^d	49.6	49.9	49.804 ^d , 49.58 ^b , 49.6 ^c
CF ₄	261.6	261.8	261.41 ^a , 261.454 ^b , 261.6 ^c , 261.419 ± 0.25 ^d	61.2	61.6	61.054 ^d , 61.05 ^b , 61.1 ^c
CHF	223.1	223.2	223.35 ^a , 234.87 ^b , 223.35 ± 0.21 ^d	34.4	34.5	34.604 ^d , 34.6 ^b
CH ₂ F	235.4	236.1		39.8	40.6	
CH ₃ F	222.4	222.6	222.84 ^a , 222.822 ^b , 222.9 ^c , 222.843 ^d	37.0	37.3	37.5 ^d , 37.5 ^b , 37.5 ^c
CHF ₂	255.9	256.1		41.8	42.1	
CH ₂ F ₂	246.4	246.6	246.7 ^a , 246.707 ^b , 246.7 ^c , 246.698 ± 0.04 ^d	42.4	42.8	42.859 ^d , 42.88 ^b , 42.9 ^c
CHF ₃	259.5	259.8	259.65 ^a , 259.674 ^b , 259.7 ^c , 259.657 ± 0.34 ^d	50.7	51.2	51.04 ^d , 51.07 ^b , 51 ^c
CCl	219.2 (224.5)	219.0 (224.3)	224.52 ^a , 224.553 ^b , 224.52 ± 0.4 ^d	31.5 (32.3)	31.5 (32.3)	32.254 ^d , 32.27 ^b
CCl ₂	265.2	265.1	265.33 ^a , 265.346 ^b , 265.346 ^d	46.6	46.7	46.249 ^d , 46.25 ^b
CCl ₃	301.7	301.9	296.83 ^a , 303.235 ^b , 296.83 ± 6.3 ^d	64.4	64.6	63.649 ^d , 63.52 ^b
CCl ₄	310.4	310.7	309.65 ^a , 309.461 ^b , 309.809 ± 0.04 ^d	84.0	84.4	83.401 ^d , 82.89 ^b , 83.3 ^c
CHCl	234.9	234.7	234.91 ^a , 234.91 ± 0.21 ^d	36.8	36.8	36.737 ^d
CH ₂ Cl	261.6	246.9		46.0	45.4	
CH ₃ Cl	234.2	234.2	234.36 ^a , 234.392 ^b , 234.6 ^c , 234.367 ± 0.42 ^d	40.7	40.7	40.731 ^d , 40.74 ^b , 40.8 ^c
CHCl ₂	281.0	281.6		51.8	52.4	
CH ₂ Cl ₂	270.4	270.4	270.28 ^a , 270.36 ^b , 270.2 ^c , 270.293 ± 0.04 ^d	51.2	51.3	50.896 ^d , 50.95 ^b , 51 ^c
CHCl ₃	296.1	296.2	295.61 ^a , 296.353 ^b , 295.7 ^c , 295.62 ± 0.04 ^d	66.0	66.2	65.383 ^d , 66.85 ^b , 65.7 ^c
CBr	230.8 (233.4)	-	233.47 ^a , 233.45 ^d	32.5 (36.1)	-	36.041 ^d
CBr ₂	288.8	-		49.4	-	
CBr ₃	337.4	-		69.6	-	
CBr ₄	358.4	-	358 ^a , 358.057 ^b , 358.1 ^c , 358.095 ^d	91.9	-	91.18 ^d , 90.96 ^b , 91.2 ^c
CHBr	246.5	-		38.0	-	
CH ₂ Br	265.0	-		46.9	-	
CH ₃ Br	245.8	-	245.913 ^b , 246.4 ^c	42.4	-	42.45 ^b , 42.4 ^c
CHBr ₂	304.2	-		54.9	-	
CH ₂ Br ₂	293.7	-	293.426 ^b , 293.2 ^c	54.7	-	54.58 ^b , 54.7 ^c
CHBr ₃	331.6	-	330.669 ^b , 330.9 ^c	71.6	-	70.99 ^b , 71.2 ^c

^aNIST-Chemistry WebBook database (experiments)⁶⁰; ^bNIST-CCCBDB database (experiments)⁴⁰; ^cCRC database⁸; ^dNIST-JANAF database, 1998.⁶

the computational data from literature,^{25–32} which confirm reliability of our calculation results for the Si-H-X and C-H-X compounds for F and Cl. Despite lacking in scalar relativistic effects, we believe the G4 to be reliable enough for predicting the properties of Si-H-Br and C-H-Br, which are confirmed by the ΔH_f° of CH₂Br, CH₃Br, SiH₂Br and SiH₃Br reported by Feller et al.²⁵ and Grant and Dixon.³²

Entropies and heat capacities at 298 K.—The entropies (S^{298}) and heat capacities (C_p^{298}) at 298 K derived from the G4 and WIRO unscaled harmonic frequencies are presented in Table V in comparison to the reported data from databases and literatures. The inclusion of low-lying electronically excited states into the electronic partition function contributes to S^{298} (in J mol⁻¹K⁻¹) with 5.3 for SiH; 5.2 for SiF; 4.8 for SiCl; 3.0 for SiBr; 5.7 for CH; 5.6 for CF; 5.3 for CCl and 2.6 for CBr and to C_p^{298} (in J mol⁻¹K⁻¹) with 0.88 for SiH; 1.09 for SiF; 1.63 for SiCl; 3.51 for SiBr; 0.04 for CH; 0.28 for CF; 0.81 for CCl and 3.63 for CBr. The effects are thus non-negligible for diatomic species.

Absolute enthalpies (ΔH^T), entropies (S^T) and heat capacities (C_p^T) at 298–2500 K.—Coefficients of 7-term NASA polynomials derived from the ΔH^T , S^T and C_p^T are provided in supplementary materials. The SOC effects are included in the ΔH^T , S^T and C_p^T for all diatomic cases. The fitting has constrained the low (high) temperature branch to reproduce the exact theoretical data at 298 K (1000 K), and thus allows creations of small discontinuities at 1000 K, which are less than ~ 0.005 kJ · mol⁻¹ for ΔH^T and less than ~ 0.03 J · mol⁻¹ · K⁻¹ for S^T and C_p^T for both the G4 and WIRO.

Conclusions

Thermochemical properties of the Si-H-X and C-H-X systems where X being F, Cl and Br have been calculated using the Gaussian 4 theory (G4) and Weizman-I theory as modified by Barnes et al. 2009 (WIRO). The calculated atomization energies were used to obtain enthalpies of formation for the complete set of molecules ($2 \times 3 \times 10 = 60$ species). The effects of low-lying electronically excited states due to spin orbit couplings (SOCs) were included for all atoms and diatomic species by mean of electronic partition function derived from the experimental or computational energy splittings. The enthalpies of formation, entropies and heat capacities were observed to be reliable in comparison to the literature. The thermochemical properties for the temperature range of 298–2500 K in the form of 7-coefficient NASA polynomials are provided as supplementary materials.

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