

Evaluation of the Thermodynamic Data of $\text{C}_2\text{H}_3\text{SiCl}_3$ Based on Quantum Chemistry Calculations

Qingfeng Zeng, Kehe Su, Litong Zhang, Yongdong Xu, Laifei Cheng, and Xiutian Yan

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Evaluation of the Thermodynamic Data of CH_3SiCl_3 Based on Quantum Chemistry Calculations

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CH_3SiCl_3 (methyltrichlorosilane) (MTS) is one of the most important precursors for manufacturing both an oxidation resistant SiC coating and a functional SiC film by chemical vapor deposition (CVD). In order to analyze the decomposition products of MTS with a thermodynamic calculation, correct thermodynamic data must be obtained from the authoritative data sources. G3(MP2) has been applied to evaluate the thermodynamic data of MTS(gas). The calculated value of the Gibbs energy of formation, $\Delta_f G_m^0(298.15 \text{ K}) = -490.13 \text{ kJ} \cdot \text{mol}^{-1}$, compares with a value, $\Delta_f G_m^0(298.15 \text{ K}) = -468.02 \text{ kJ} \cdot \text{mol}^{-1}$ from the 4th edition of the NIST-JANAF Thermochemical Tables. Further analyses have been conducted: (1) by using G3, G3//B3LYP, and G3(MP2)//B3LYP theories; (2) by using variable scale factors for G3(MP2) theory; and (3) by investigating the accuracy of both experimental and calculated thermodynamic data. The calculated values can provide $\Delta_f G_m^0$ values for MTS above 1500 K. The final fitted equation for MTS(gas) is: $\Delta_f G_m^0 = 7.5763 \times 10^{-6} T^2 + 1.9649 \times 10^{-1} T - 5.4817 \times 10^2$, where T is absolute temperature. © 2006 American Institute of Physics.

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Key words: CH_3SiCl_3 ; G3 theories; G3MP2; Gibbs free energy; quantum chemistry.

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1. Introduction

Silicon carbide (SiC) is an attractive material for structural and functional applications because of its prominent properties such as excellent hardness, chemical resistance at high temperatures, wide energy band gap, high electrical mobility, and thermal stability.^{1–3} Methyltrichlorosilane (Cl_3SiCH_3) (MTS) is frequently used as a source precursor for chemical vapor depositing high quality stoichiometric SiC films because of its equivalent ratio of Si to C.^{4–6} In testing a new chemical vapor deposition (CVD) system, thermodynamic calculations are generally carried out to predict the final composition of the system at equilibrium and to understand the influence of many parameters such as temperature, pressure, and inlet gas flux. At a high temperature and a low flow rate, near equilibrium conditions are actually reached when the chemical kinetics are intrinsically faster than the mass transfer step. Such calculations have been investigated by several groups by using atomic mass balances and minimizing the overall Gibbs energy. In most of these calculations, the thermodynamic data were taken from the 3rd edition of the JANAF Thermochemical Tables.^{7–9}

However, the $\Delta_f G_m^0(T)$ values for MTS(g) in the 3rd edition of the JANAF Thermochemical Tables¹⁰ are quite different from that in the 4th edition of the NIST-JANAF Thermochemical Tables,¹¹ as shown in Fig. 1. In Sec. 7 (p. 19) of the 4th edition, a statement was made as to calculation error

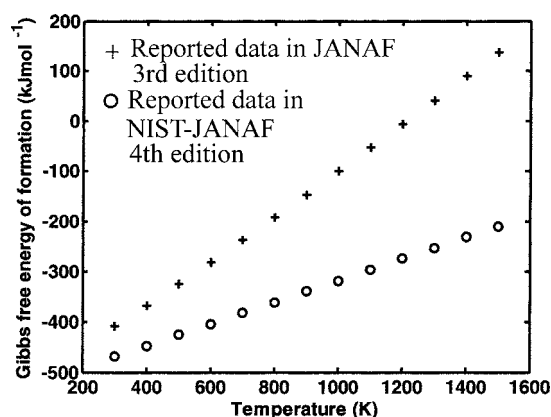


Fig. 1. Gibbs free energy of formation for MTS(g) in the JANAF Thermochemical Tables.

in the formation properties of MTS(g) in the 3rd edition. The 4th edition values for the formation properties are simply recalculated (correct) values based on the same enthalpy of formation.

The JANAF evaluation was performed in December 1960. The enthalpy of formation values is listed as “source unknown,” so that this value is not known to be based on experiment or theory. The heat capacity values are stated as taken from a 1960 Rensselaer Polytechnic Institute publication by Janz. Again, there is not any definitive information here as to the origin of these values—experiment or theory. We will refer to these values as reported values (rather than experimental or theoretical).

It is necessary to use an independent method, either another experimental value or a reliable computational calculation, to evaluate the thermodynamic data of MTS(g). This paper will carry out the later approach.

Owing to the contributions of Pople, the properties of molecules can be calculated and are often used to illustrate or explain the results of different of experiments.¹² G3(MP2), one of the accurate quantum chemistry calculation methods, has been proven to calculate the thermodynamic data such as ionization potentials, electron affinities, proton affinities, and enthalpies of formation with an average absolute deviation less than $2\text{ kcal}\cdot\text{mol}^{-1}$.¹³ This paper uses this method to calculate the thermodynamic data of MTS(g) and to determine more reliable $\Delta_f G_m^0(T)$ values for MTS(gas). Furthermore, since both editions of the JANAF Thermochemical Tables only provide $\Delta_f G_m^0(T)$ values for MTS(g) at temperatures between 298.15 and 1500 K, the calculations, on the other hand, can provide data above 1500 K.

2. Calculation Methods

2.1. Descriptions of G3(MP2) Theory

G3(MP2) theory belongs to the Gaussian-n series of model chemistries which aim to calculate molecular energies to high accuracy.^{13–15} G3(MP2) is a variation of G3 theory, which uses second-order Møller–Plesset (MP2) instead of fourth-order Møller–Plesset (MP4) to calculate the single point energy. The energy is first obtained by a higher level calculation at the quadratic configuration interaction level of theory with the 6-31G(d) basis set, i.e., QCISD(T)/6-31G(d). This energy is then modified by a series of corrections to obtain a total energy, E_0 , as Eq. (1) shows¹³

$$E_0[\text{G3(MP2)}] = \text{QCISD(T)/6-31G(d)} + \Delta E_{\text{MP2}} + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}). \quad (1)$$

The correction at the second-order Møller–Plesset level (MP2) is given by Eq. (2).

$$\Delta E_{\text{MP2}} = [E(\text{MP2/G3MP2 large})] - [E(\text{MP2/6-31G(d)})] \quad (2)$$

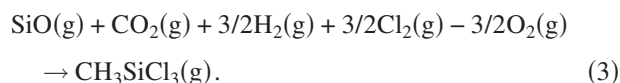
$\Delta E(\text{SO})$ is spin-orbit correction; $E(\text{HLC})$ is a higher level correction to take into account remaining deficiencies in the energy calculations; and $E(\text{ZPE})$ is zero-point correction,

which obtained from scaled (0.8929) HF/6-31G(d) frequencies.

The average absolute deviation from experiment of G3 theory for the 299 energies from the G2/97 test set^{16,17} is 5.12 kJ·mol⁻¹ (0.94 kcal·mol⁻¹) and for the subset of 148 neutral enthalpies it is 4.27 kJ·mol⁻¹ (1.02 kcal·mol⁻¹). For G3(MP2) theory, the absolute deviations are 5.44 kJ·mol⁻¹ (1.30 kcal·mol⁻¹) and 4.94 kJ·mol⁻¹ (1.18 kcal·mol⁻¹) for the above cases. The computational cost of G3(MP2) theory, however, is much less than that of G3 theory. For benzene, G3(MP2) theory is about eight times faster than G3 theory in single point energy calculations. More detailed description can be found in Curtiss *et al.*¹³

2.2. Calculation for Gibbs Free Energy of Formation

Equation (3) is a virtual chemical reaction



Small and ordinary molecules, selected from the G2/97 test set, are considered as the reactants because of the guaranteed accuracy for G3MP2 theory.¹³ As long as $\Delta_f G_m^0(T)$ for the reactants are known, $\Delta_f G_m^0(T)$ for MTS can be obtained from Eq. (4). The $\Delta_f G_m^0(T)$ for the reactants are taken from the 4th edition of the NIST-JANAF Thermochemical Tables

$$\Delta_f G_m^0(\text{MTS}, T) = \Delta_r G_m^0 + \sum_i \nu_i(\text{reactant}) \Delta_f G_m^0(\text{reactant}, T). \quad (4)$$

Here, ν_i is the mole number corresponding to species i and $\Delta_r G_m^0(T)$ is the Gibbs free energy of the reaction, which can be obtained from Eq. (5)

$$\Delta_r G_m^0 = \left(\sum_i \nu_i H_m^0(298.15) + \int_{298.15}^T \sum_i \nu_i C_p dT \right) - T \left(\sum_i \nu_i S_m^0(298.15) + \int_{298.15}^T \sum_i \frac{\nu_i C_p}{T} dT \right). \quad (5)$$

$H_m^0(298.15 \text{ K})$ and $S_m^0(298.15 \text{ K})$ are standard enthalpy and entropy at 298.15 K, respectively, which can be obtained from the high level model chemistry calculation based on G3(MP2) theory. T is an absolute temperature and C_p is the heat capacity, which is the function of vibration frequency for multiatom molecules, as Eqs. (6)–(8) show.

For a single atom,

$$C_p = \frac{5}{2}R \quad (6)$$

for linear molecules

$$C_p = R \left[\frac{7}{2} + \sum_{i=1}^{3n-5} (\theta_i/T)^2 e^{\theta_i/T} (e^{\theta_i/T} - 1)^{-2} \right] \quad (7)$$

and for nonlinear molecules

TABLE 1. Calculated enthalpies and Gibbs free energy at 298.15 K

SiO(g) + CO ₂ (g) + 3/2H ₂ (g) + 3/2Cl ₂ (g) - 3/2O ₂ (g) → MTS(g)		
Species	H (Hartree)	G (Hartree)
MTS (C _{3v})	-1708.328187	-1708.368173
SiO (C _v)	-364.230511	-364.254488
CO ₂ (D _h)	-188.375266	-188.399500
H ₂ (D _h)	-1.166831	-1.181590
Cl ₂ (D _h)	-919.461443	-919.486741
O ₂ (³ D _h)	-150.161030	-150.184241

$$C_p = R \left[4 + \sum_{i=1}^{3n-6} (\theta_i/T)^2 e^{\theta_i/T} (e^{\theta_i/T} - 1)^{-2} \right] \quad (8)$$

$$\theta_i = h\nu_i/k, \quad (9)$$

where R is the universal gas constant (J·K⁻¹·mol⁻¹), n is the number of atoms in the system, θ_i is the vibration temperature (K), h is Planck's constant (J·s), ν_i is vibration frequency (s⁻¹), and k is Boltzmann constant (J·K⁻¹).

3. Results and Discussion

3.1. Entropy and Heat Capacity for the Species

Table 1 shows the values calculated from Gaussian 03W¹⁸ for reaction (3). All values are in Hartrees.

The accuracy of G3MP2 can be initially evaluated by comparing entropies obtained from Eq. (10) and experimental results

$$S = \frac{H - G}{298.15}. \quad (10)$$

From Table 2, it is found that G3MP2 is very accurate. The maximum absolute error and relative error between experimental values and calculated values are 0.97 J·K⁻¹ mol⁻¹ and 0.54%, respectively. The comparisons of both heat capacity and entropy for MTS(g) in the whole temperature range are drawn in Figs. 2(a) and 2(b), respectively. From Figs. 2(a) and 2(b), the calculated values fit experimental (reported) values very well even up to 1500 K. The experiment (reported) values fall between the ±5% boundary lines for the calculated curves.

TABLE 2. Reported and calculated values for entropies at 298.15 K

S° (J·K ⁻¹ ·mol ⁻¹)				
Species	Reported	Calculated	Rep-Calc	Relative error(%)
MTS(g)	351.15	352.12	0.97	0.28
SiO(g)	211.58	211.14	0.44	0.21
CO ₂ (g)	213.80	213.40	0.40	0.19
H ₂ (g)	130.68	129.97	0.71	0.54
Cl ₂ (g)	223.08	222.77	0.31	0.14
O ₂ (g)	205.15	204.40	0.75	0.37

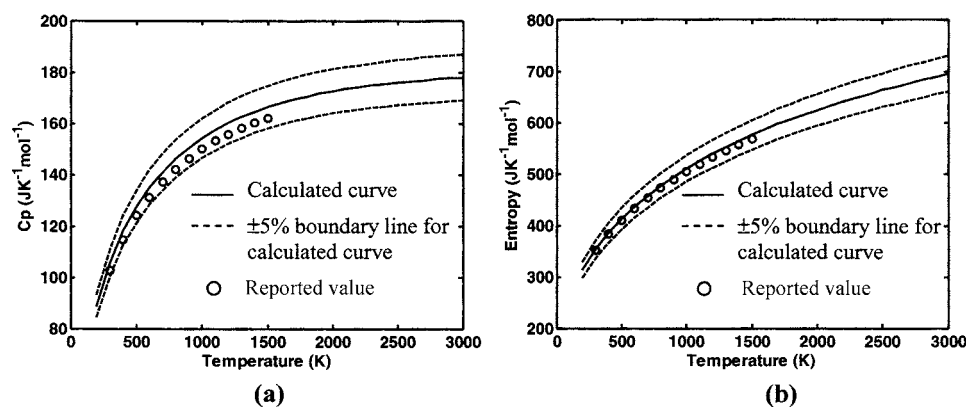


FIG. 2. Heat capacity (a) and entropy (b) for MTS(g).

3.2. Gibbs Free Energy of Formation

In examining the MTS–H₂ system, the 4th edition of the NIST-JANAF Thermochemical Tables was used. The 4th edition is the updated version of the 3rd edition and contains the corrected calculations for the formation properties of MTS(g). Since the origin of the enthalpy of formation for MTS(g) in this critical evaluation is unknown, it is necessary to investigate the accuracy of this value. The G3MP2 calculation is conducted. The final results are shown in Fig. 3.

The data in the NIST-JANAF 4th edition are close to the calculated values. The calculated value of $\Delta_f G_m^0$ at 298.15 K is $-490.13 \text{ kJ} \cdot \text{mol}^{-1}$, and $-468.02 \text{ kJ} \cdot \text{mol}^{-1}$ in the 4th edition of NIST-JANAF. The calculated value of $\Delta_f G_m^0$ at 1400 K is $-258.31 \text{ kJ} \cdot \text{mol}^{-1}$, which is $-231.63 \text{ kJ} \cdot \text{mol}^{-1}$ in the 4th edition of NIST-JANAF.

The 4th edition of the NIST-JANAF Thermochemical Tables only provides the $\Delta_f G_m^0(T)$ value for MTS(g) at temperatures between 298.15 and 1500 K. The calculated values can provide $\Delta_f G_m^0(T)$ values for MTS(g) above 1500 K. The final fitted equation of $\Delta_f G_m^0$ for MTS(gas) is shown in Eq. (11a):

$$\Delta_f G_m^0(\text{MTS}, g, T) = 7.5763 \times 10^{-6} T^2 + 1.9649 \times 10^{-1} T - 5.4817 \times 10^2. \quad (11a)$$

In Fig. 3, below 500 K, the data in the 4th edition of the

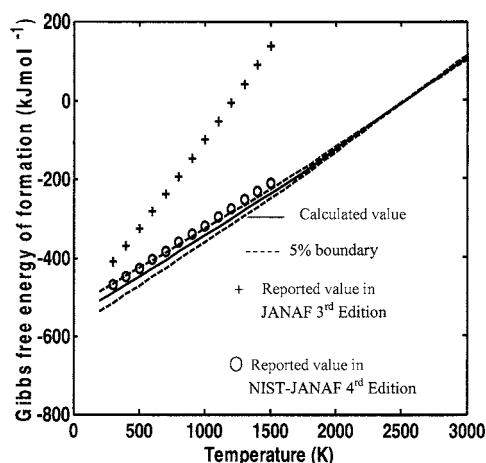


FIG. 3. Gibbs free energy of formation for MTS(g).

NIST-JANAF locate between the $\pm 5\%$ boundary lines for the calculated curve. Above 500 K, the experimental (reported) data in the 4th edition of NIST-JANAF are a little higher than $\pm 5\%$ boundary line. The maximum absolute error between the calculated values and the experimental data in the 4th edition of NIST-JANAF is $27.25 \text{ kJ} \cdot \text{mol}^{-1}$ at 1500 K. The minimum absolute error between the calculated values and the experimental data in the NIST-JANAF 4th edition is $22.11 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

Further analyses have been conducted in order to determine the factors that caused the difference between the calculated values and the experimental (reported) values in the 4th edition of NIST-JANAF.

First, this difference might result from the accuracy of G3MP2. It is reported that the average absolute deviations from the experiment for the 299 energies in the G2/97 test set are $4.14 \text{ kJ} \cdot \text{mol}^{-1}$ ($0.99 \text{ kcal} \cdot \text{mol}^{-1}$) for G3//B3LYP, $5.23 \text{ kJ} \cdot \text{mol}^{-1}$ ($1.25 \text{ kcal} \cdot \text{mol}^{-1}$) for G3(MP2)//B3LYP, $4.27 \text{ kJ} \cdot \text{mol}^{-1}$ ($1.02 \text{ kcal} \cdot \text{mol}^{-1}$) for G3, and $5.44 \text{ kJ} \cdot \text{mol}^{-1}$ ($1.30 \text{ kcal} \cdot \text{mol}^{-1}$) for G3(MP2). $\Delta_f G_m^0$ for MTS were further calculated by using G3//B3LYP, G3MP2//B3LYP, and G3 theories at temperatures from 300 to 1500 K. A scale factor of 0.96 was used for B3LYP/6-1G(d) as the recommendation in Anwar *et al.*¹⁵ However, the errors between the calculations and experiments still exist, as Fig. 4 shows. In fact, G3(MP2) has the minimum average error for calculating $\Delta_f G_m^0$ for MTS(g). Generally, the accuracy sequence of G3 theories for the 299 energies from high level to low level is G3//B3LYP, G3, G3(MP2)//B3LYP, and G3(MP2). It is not always true for a specific case. Here, the calculation of $\Delta_f G_m^0$ for MTS(g) is an example.

Another reason that might cause the error between the calculations and the experiments is the scale factor for zero-point energies and frequencies. Variable scale factors have been applied for specific calculations. As Anwar *et al.*¹⁵ mentioned, the scale factor has a surprisingly large effect on the accuracy of the B3LYP method, and is probably compensating for some other deficiency in the density functional method. It is the same for other quantum chemical methods.^{13,14,19} Different scale factors were applied by using G3(MP2) theory to further calculate the $\Delta_f G_m^0$ for MTS(g), as Fig. 5 shows.

In Fig. 5, although a wide range of scale factors were used

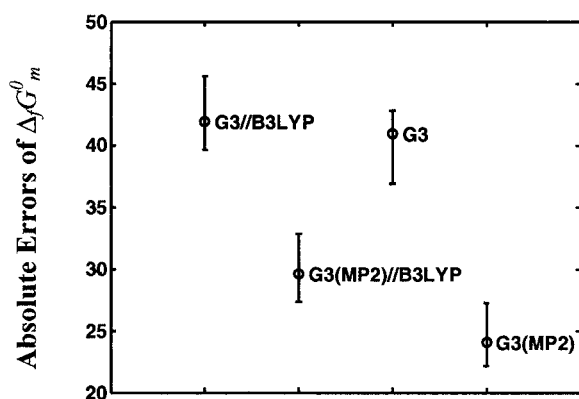


FIG. 4. The absolute errors of $\Delta_f G_m^0$ between the experiments and calculations for MTS(g) obtained by using G3 theories.

in the further calculations, the errors of $\Delta_f G_m^0$ between the experiments and calculations were not satisfactorily improved. The minimum average error was $12.24 \text{ kJ} \cdot \text{mol}^{-1}$ at a scale factor of 1.8. However, such a big scale factor is incredible.

According to above endeavors of finding the potential reasons that might cause the errors of $\Delta_f G_m^0$ between the calculations and experiments, it is neither because of the deficiency of G3(MP2) theory, nor because an uncertain scale factor was used. There might be something wrong with the theories or the experiments.

Let us go back to Eqs. (3) and (4). There is no doubt that the $\Delta_f G_m^0$ for the reactants on the left side of Eq. (3). The reason is very simple: the $\Delta_f G_m^0$ Cl₂, H₂, and O₂ definitely equals zero in the whole temperature range; SiO and CO₂ have been widely investigated and their experimental thermodynamic data have been looking for reference data to evaluate theoretical calculations.¹⁷ As a result, $\Delta_r G_m$ should be investigated in the next stage.

$\Delta_r G_m^0$ can be obtained from Eq. (5). Equation (5) can be rewritten as Eq. (11b).

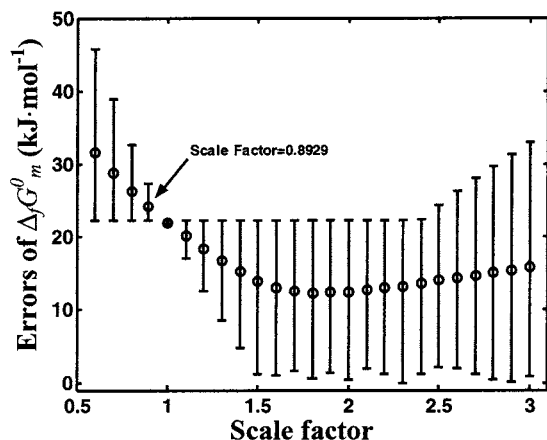


FIG. 5. The errors of $\Delta_f G_m^0$ between the reported values and calculations for MTS(g) obtained by using G3(MP2) theory with different scale factors.

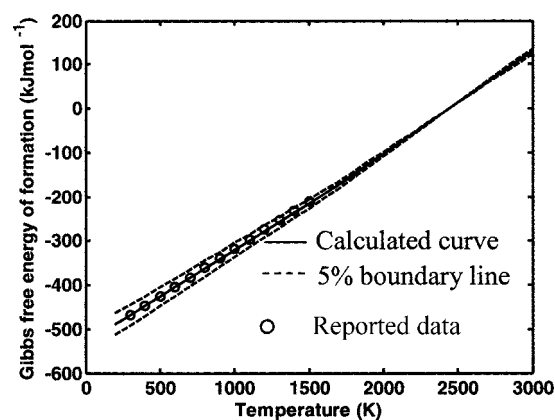


FIG. 6. $\Delta_f G_m^0$ for MTS(g) by using $\Delta_r H_m^0(298.15 \text{ K})$ obtained from NIST-JANAF Thermochemical Table.

$$\Delta_r G_m^0 = \Delta_r H_m^0(298.15) - T\Delta_r S_m^0(298.15) + \int_{298.15}^T \sum_i \nu_i C_p dT + \int_{298.15}^T \sum_i \frac{\nu_i C_p}{T} dT. \quad (11b)$$

In Eq. (11b), there are three possible objects: $\Delta_r H_m^0(298.15)$, $\Delta_r S_m^0(298.15)$, and C_p , which might result in the errors between the calculations and experiments. It has been proved that C_p for all of the species including MTS meet with the experiments very well. $\Delta_r H_m^0(298.15)$ and $\Delta_r S_m^0(298.15)$ were calculated by using both G3 theories and experimental (reported) data in the 4th edition of NIST-JANAF, as Table 3 shows. The calculated value and experimental value for $\Delta_r H_m^0(298.15 \text{ K})$ were obtained from Eqs. (12) and (13), respectively.

$$\Delta_r H_m^0(298.15 \text{ K}) = H_m^0(\text{MTS}, 298.15 \text{ K}) - \sum_i \nu_i(\text{reactant}) H_m^0(\text{reactant}) \quad (12)$$

$$\Delta_r H_m^0(298.15 \text{ K}) = \Delta_f H_m^0(\text{MTS}, 298.15 \text{ K}) - \sum_i \nu_i(\text{reactant}) \Delta_f H_m^0(\text{reactant}). \quad (13)$$

From Table 3, it is easy to know that $\Delta_r H_m^0(298.15 \text{ K})$ caused the difference between calculations and experiments. Figure 6 shows the new results that were obtained by using the experimental value of $-34.92 \text{ kJ} \cdot \text{mol}^{-1}$ for $\Delta_r H_m^0(298.15 \text{ K})$ in G3(MP2) calculation.

In Eq. (12), the enthalpy energies for the reactants, SiO, CO₂, O₂, H₂, and Cl₂, have been proved by the G2/97 test set. The $H_m^0(\text{MTS}, 298.15)$ has already been used to calculate the entropy and heat capacity for MTS, and the calculated values fit the experimental values very well.

TABLE 3. $\Delta_f H_m^0(298.15 \text{ K})$ and $\Delta_f S_m^0(298.15 \text{ K})$ obtained from G3 theories and experimental data

	G3	G3(MP2)	G3//B3LYP	G3(MP2)//B3LYP	NIST-JANAF 4th edition
$\Delta_f H_m^0(298.15 \text{ K})$ (kJ·mol ⁻¹)	-72.65	-56.56	-73.87	-61.63	-34.92
$\Delta_f S_m^0(298.15 \text{ K})$ (J·K ⁻¹ ·mol ⁻¹)	-296.18	-296.18	-295.73	-295.73	-297.15

In Eq. (13), the experimental enthalpies of formation for the reactants, SiO, CO₂, O₂, H₂, and Cl₂, have been proved to be accurate.¹⁷ As a result, the enthalpy of formation for MTS, i.e., $\Delta_f H_m^0(\text{MTS}, 298.15 \text{ K})$, is the only factor that might cause the difference between calculations and experiments.

Furthermore, from Table 3, G3 theories seem to be making a systematic mistake, because all of the calculated $\Delta_f H_m^0(298.15 \text{ K})$ are relatively higher than the reported (experimental?) value. It is known that these experimental (reported) values were obtained in the 1960s and no further reports on these data have been published so far. If we suppose that, at least at a temperature of 298.15 K, the G3 theories are correct for calculating enthalpy energy, then the experimental data should be measured.

4. Conclusion

G3 theories have been applied to investigate the thermodynamic data for MTS(g), while G3(MP2) has the minimum average error between the calculations and reported data at a temperature range from 300 to 1500 K. The Gibbs free energy, an important parameter for thermodynamic calculations in the MTS-H₂ system, was derived and its temperature dependence is shown in Eq. (11a).

There is a difference between the calculated values and the values (experimental or theoretical origin is not known) reported in the 4th edition of NIST-JANAF.¹¹ It is found that enthalpy of reaction at 298.15 K caused this difference. Furthermore, this error was not improved by using G3, G3//B3LYP, and G3(MP2)//B3LYP theories. A variety of scale factors for G3(MP2) have been investigated as well, but the difference still exists. It is suggested that the experimental data of $\Delta_f H_m^0(298.15 \text{ K})$ for MTS(g) should be measured. At the same time, the heat capacity should be measured.

5. Acknowledgments

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