

# Thermochemical Properties of $\text{Si}_2\text{F}_6$ and $\text{SiF}_4$ in Gas and Condensed Phases

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The available data for determining the thermochemical parameters for  $\text{Si}_2\text{F}_6$  and  $\text{SiF}_4$  has been assembled. With this information, the thermochemical functions for  $\text{Si}_2\text{F}_6$  and  $\text{SiF}_4$  have been calculated as ideal gases in the harmonic oscillator approximation. These results are presented in the format of the NIST–JANAF Thermochemical Tables, as well as in the format of the CHEMKIN Thermochemical Database. Using the vapor pressure data, the thermochemical parameters for  $\text{Si}_2\text{F}_6$  in the solid phase and  $\text{SiF}_4$  in both the solid and liquid phases have been calculated. These results are compared with available experimental and calculated data. The earlier results are in good agreement with our results. However, the  $\text{Si}_2\text{F}_6$  results were not previously available in the JANAF format, and the results for both species are on a much firmer footing with the new experimental data we used. The anharmonicity constants measured earlier for  $\text{SiF}_4$  permitted a determination of the effect of anharmonicity on the thermochemical properties for this species. For this species at least, the harmonic oscillator approximation is very good. Differences between the harmonic and anharmonic calculations were only significant at temperatures above 1000 K. © 2001 American Institute of Physics.

Key words: disilicon tetrafluoride; enthalpy; entropy; heat capacity; silicon tetrafluoride; thermochemical functions; vapor pressure.

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## 1. Introduction

The thermal and photochemical reactions of Si<sub>2</sub>F<sub>6</sub> have received attention in recent years because of the potential use of the molecule in some significant applications. The first of

these is as a reagent for deposition of thin films of silicon,<sup>1–4</sup> while the second is silicon isotope separation by infrared multiple-photon dissociation.<sup>5–9</sup> This species has also been recognized as a photolytic source of SiF<sub>2</sub>.<sup>10,11</sup> Information is available on the thermochemical functions of this species, but more recent spectroscopic data on the Si<sub>2</sub>F<sub>6</sub> molecule suggests an improved calculation of its thermochemical functions. The thermochemical functions are essential for any chemical kinetic or equilibrium modeling of chemical processes involving this species.

The species SiF<sub>4</sub> also has many applications. The most important application is a silicon source for chemical vapor deposition.<sup>12</sup> It is also a product of many reactions of Si<sub>2</sub>F<sub>6</sub>. These applications and reactions make knowledge of its thermochemical functions essential as well. Its thermochemistry is reasonably well understood, but some precise spectroscopic<sup>13</sup> and calorimetric<sup>14</sup> measurements, reported since the previous evaluations were made, make possible a confirmation of the thermochemical functions.

The information necessary for calculation of the complete sets of thermochemical functions for the gas phases of these species in the harmonic oscillator approximation includes: molecular weight of the species; structure (or rotational constants) of the molecule; enthalpy of formation of the species at one temperature; complete set of fundamental vibrational frequencies for the species; rotational symmetry for the molecule; internal rotation barrier when one exists; standard state entropy of the constituent atoms; and standard state enthalpy of the constituent atoms.

Another potential contributor to the thermochemical parameters is electronically excited states of the molecules. Neither of these two species have any low-lying electronic states, so no contribution of electronic states is included. The calculation of the temperature dependence of the parameters for polyatomic molecules normally relies on the harmonic oscillator approximation. The reason for the use of this approximation is: first, it seems to work well; second, the statistical mechanical expressions for the temperature dependence of heat capacity, entropy, and enthalpy are particularly simple (see Sec. 3.1); third, complete sets anharmonicity constants (second order) are available for only a few larger molecules. The species SiF<sub>4</sub> is one of those for which those constants have been measured. One can take the calculation of the thermochemical functions for this species to the next level of approximation by calculating them directly from their definition in terms of the vibrational partition function. We do this in Sec. 5.3. This calculation not only provides an estimation of the effect of molecular anharmonicity on those functions, but also allows us to evaluate the correctness of the harmonic oscillator approximation for polyatomic molecules. Calculation of the effect of anharmonicity on the thermochemical functions requires the complete list enumerated above for the harmonic oscillator approximation, plus the complete set of anharmonicity constants, including all cross terms.

Less information is available on the thermochemical functions of the condensed phases of these two species. The gas

phase functions, in connection with available vapor pressure data, allow the estimation of the entropy and enthalpy of formation for the condensed phases of these two silicon fluorides. Some experimental heat capacity data is also available for both the solid<sup>15</sup> and liquid<sup>16</sup> phases of SiF<sub>4</sub>.

## 2. Current Status of Experimental and Theoretical Data

### 2.1. Disilicon Tetrafluoride

Ho and Melius<sup>17</sup> have calculated the enthalpy of formation for Si<sub>2</sub>F<sub>6</sub> at 298.15 K. Two other calculations<sup>18,19</sup> are consistent with that value. They have also reported the entropy, the heat capacity, and the temperature dependence of the Gibbs energy of the molecule. These were based on their own calculation of bond strengths and fundamental vibrational frequencies for Si<sub>2</sub>F<sub>6</sub>. Some of the fundamental vibrational frequencies for Si<sub>2</sub>F<sub>6</sub> were available from earlier experimental measurements. The more recent work of Tosa *et al.*<sup>20,21</sup> gives a complete experimental set of accurate values of these frequencies. These make possible the calculation of accurate thermochemical parameters for the ideal gas in the harmonic oscillator approximation. The latter paper<sup>21</sup> also has a suggested height for the barrier to internal rotation about the Si–Si bond of Si<sub>2</sub>F<sub>6</sub>. The hindered rotation influences the heat capacity, entropy, and other thermochemical parameters. That barrier (6.34 ± 0.24 kJ/mol) is substantially higher than an earlier electron diffraction measurement<sup>22</sup> (2.59 ± 0.46 kJ/mol). It is also substantially lower than a calculation of the barrier in the same paper (10.04 ± 0.84 kJ/mol) using the CNDO/2 approximation.<sup>22</sup> We use the value for the barrier height suggested by Tosa *et al.*<sup>21</sup> The thermochemical parameters for Si<sub>2</sub>F<sub>6</sub> may also be calculated from the constants available in the THERMO.DAT file of the CHEMKIN database.<sup>23</sup> The information in that database probably came from the calculations of Ho and Melius.<sup>17</sup> Melius was at the Combustion Research Laboratory, Sandia Livermore National Laboratory, when the paper was published, which is the organization that produced CHEMKIN. The National Institute of Science and Technology (NIST) also has an online data source,<sup>24</sup> which has some Si<sub>2</sub>F<sub>6</sub> thermochemistry. Its source is CHEMKIN.

### 2.2. Silicon Tetrafluoride

Contrary to the situation for Si<sub>2</sub>F<sub>6</sub>, thermochemical functions for the species SiF<sub>4</sub> are available in the NIST–JANAF Thermochemical Tables.<sup>25</sup> Some additional spectroscopic measurements<sup>13</sup> have been made on that species, and a reconsideration of the effect of those measurements on the thermochemical functions is appropriate. An improved calorimetric measurement of the enthalpy of formation of SiF<sub>4</sub> has also been made.<sup>14</sup> Wise *et al.*<sup>26</sup> made the measurements of the enthalpy of formation on which the values in the current NIST–JANAF Thermochemical Tables<sup>25</sup> are based. These measurements also seem to be the major source for enthalpies of formation in other compilations.<sup>18,19</sup> They all

agree that the enthalpy of formation of SiF<sub>4</sub> at 298.15 K is the value initially measured by Wise *et al.*,<sup>26</sup> 1614.94 ± 0.79 kJ/mol. Confusion about the enthalpy of formation<sup>14</sup> of SiO<sub>2</sub> brought that value into question. Therefore, Johnson,<sup>14</sup> of the same laboratory, did another direct measurement of the enthalpy of formation of SiF<sub>4</sub> from the elements. He also had some questions about the heat produced by a reaction of fluorine during the calorimetric measurement. He made a correction for that reaction and found that the new value for the enthalpy of formation of SiF<sub>4</sub>, in the gas phase was

$$\Delta_f H^0(298.15) = (-1615.78 \pm 0.46) \text{ kJ/mol}, \quad (1)$$

which he believes to be more accurate. It still falls within the error bars of the initial measurement. This value has been accepted as the basis for our calculations of the enthalpies of formation of SiF<sub>4</sub> at all temperatures.

The infrared spectroscopic measurements and analysis for SiF<sub>4</sub> by McDowell *et al.*<sup>13</sup> not only gives accurate fundamental vibrational frequencies for the molecule, but it also gives all of the anharmonicity constants. Recently, Wang *et al.*<sup>27</sup> have calculated the structure and spectroscopic constants of SiF<sub>4</sub>, including all vibrational frequencies and anharmonicity constants. They used the highly accurate coupled-cluster single double (triple) method for these calculations. Their values are consistent with the experimental values of McDowell *et al.*<sup>13</sup> The calculated values<sup>27</sup> for the vibrational frequencies are within the experimental error bars.<sup>13</sup> Most of the anharmonicity constants are as well. Using the calculated constants<sup>27</sup> would not appreciably change the results that are presented in Sec. 5.3.

The NIST–JANAF Thermochemical Tables<sup>25</sup> also contain functions for the lower silicon fluorides: SiF<sub>3</sub>, SiF<sub>2</sub>, and SiF. Although there are some additional calculations<sup>11,21,22</sup> and measurements<sup>28</sup> of the bond strengths for these silicon fluorides, it does not appear that any recalculation of their thermochemical functions is necessary. They seem to be sufficiently accurate as they stand.

### 2.3. Condensed Phases

The condensed phases of Si<sub>2</sub>F<sub>6</sub> and SiF<sub>4</sub> are not as well understood. Some experimental information is available that allows estimation of the thermochemical parameters for the solid phase of Si<sub>2</sub>F<sub>6</sub> and both the liquid and solid phases of SiF<sub>4</sub>.

Si<sub>2</sub>F<sub>6</sub> has no liquid phase at atmospheric pressure. Consequently, we only consider the solid phase thermochemical parameters for Si<sub>2</sub>F<sub>6</sub>. Vapor pressure measurements<sup>29</sup> over the solid allow determination of the enthalpy and entropy of sublimation for the species. These in turn, with the thermochemical parameters for the ideal gas, enable us to calculate the entropy and enthalpy of formation for solid Si<sub>2</sub>F<sub>6</sub> in the temperature range near its sublimation temperature. One can obtain the heat capacity from the enthalpy function. Phase change temperatures are also available for the species.<sup>29</sup>

The liquid phase of SiF<sub>4</sub> is also nonexistent at atmospheric pressure; however, both heat capacity and vapor pressure data are available for both the solid phase and for the liquid phase at pressures higher than atmospheric. Therefore, we present thermochemical parameters for both phases. Pace and Moser<sup>15</sup> reported a careful measurement of the saturation heat capacity for SiF<sub>4</sub> from a temperature of 15 K up through the triple point and into the liquid phase. They also obtained a precise value of the triple point, 186.35 K. Touloukian and Buyco<sup>30</sup> also has a table and a graph of the constant pressure heat capacity of SiF<sub>4</sub>, which is attributed entirely to Pace and Moser;<sup>15</sup> however, the values have what appears to be an error in compiling the table which results in some of their heat capacity values being lower than those of Pace and Moser<sup>15</sup> between 83 and 152 K. This error led the authors to assign a phase transition to SiF<sub>4</sub> at 83 K. The values in Pace and Moser<sup>15</sup> are correct, those in Touloukian and Buyco<sup>30</sup> are only correct at the temperature extremes. Yaws *et al.*<sup>16</sup> have also measured the heat capacity for liquid SiF<sub>4</sub> to much higher temperatures.

The phase-change temperatures for SiF<sub>4</sub> are reported in the CRC Handbook.<sup>31</sup> However, this Handbook relies on the early work of Stull<sup>29</sup> and is not correct. The phase change temperatures of Pace and Moser<sup>15</sup> are more reliable.

Kalish and Tabachnikov<sup>32</sup> have analyzed the available vapor pressure data to 1982 for SiF<sub>4</sub> and have concluded that the most correct data are from Pace and Moser.<sup>15</sup> They also speak highly of the early work of Ruff and Asher<sup>33</sup> over solid SiF<sub>4</sub> at low temperature and that of Booth and Swinehart<sup>34</sup> at high temperature (and high pressure) over liquid SiF<sub>4</sub>. They discount the measurements of Stull,<sup>29</sup> which appear to be low in the region of the triple point. Stull<sup>29</sup> has vapor pressure measurements over a range of temperatures. These are also the data in the "Vapor Pressure" section of the CRC Handbook,<sup>31</sup> which are also incorrect. The section entitled "Sublimation Pressure of Solids" gives the sublimation pressure of SiF<sub>4</sub> over the same temperature range. These data have at least some contribution from the experiments of Pace and Moser<sup>15</sup> and appear to be much more correct. The measurements of Panode and Papish<sup>35</sup> in the temperature range near the triple point appear to be uniformly high and are probably contaminated by some volatile impurity. The much earlier compilation of vapor pressure data from the International Critical Tables<sup>36</sup> give a value for the triple point and few values of the vapor pressure of SiF<sub>4</sub>. Those agree qualitatively with later work, but they are much less precise and are not considered in this paper. We agree with the assessment of Kalish and Tabachnikov<sup>32</sup> and have used that vapor pressure information to estimate the enthalpy and entropy changes for vaporization of the condensed phases.

The CHEMKIN<sup>23</sup> chemical kinetic package has constants for calculation of thermochemical function for SiF<sub>4</sub>. These are based on the NIST–JANAF Thermochemical Tables.<sup>25</sup>

### 3. Approach

The values of the different thermochemical functions are calculated by following the procedures for polyatomic mol-

ecules in the introduction to the NIST–JANAF Thermochemical Tables.<sup>25</sup> The thermochemical functions for gaseous polyatomic molecules and statistical mechanical expressions follow. These expressions all rely on the statistical mechanical relationship between the vibrational partition function and the thermochemical functions. Statistical mechanics texts<sup>37,38</sup> give more detail on the derivation of these expressions.

### 3.1. Formulas for the Thermochemical Functions for Gas-Phase Species

#### 3.1.1. Heat Capacity

For heat capacity

$$C_p^0/R = 5/2 + 3/2 + \sum_{i=1}^n u_i^2 e^{-u_i} / (1 - e^{-u_i})^2. \quad (2)$$

The first term is the translational contribution; the second, the rotational contribution; and the third, the vibrational contribution.  $R$  is the gas constant; the sum is over each of the  $n$  vibrational modes of the molecule; and  $u_i$  for each vibrational mode is

$$u_i = c_2 v_i / T. \quad (3)$$

The constant  $c_2 = hc/k = 1.4387645$ , and  $v_i$  is the fundamental vibrational frequency (wave number) of the  $i$ th mode.

#### 3.1.2. Enthalpy

The temperature dependence of the enthalpy is a similar expression

$$\begin{aligned} [H^0(T) - H^0(298.15)]/RT \\ = 5/2 + 3/2 + \sum_{i=1}^n u_i e^{-u_i} / (1 - e^{-u_i}). \end{aligned} \quad (4)$$

#### 3.1.3. Entropy

For entropy, the translation contribution is

$$S_r^0/R = 3/2 \ln M_r + 5/2 \ln T + \ln k/p^0 (2\pi k/Nh^2)^{3/2}, \quad (5)$$

where  $M_r$  is the molecular weight,  $k$  is the Boltzmann constant,  $p^0$  is the standard state pressure (0.1 MPa), and  $h$  is Planck's constant. The rotational contribution is

$$S_r^0/R = 3/2 + 3/2 \ln T + 1/2 \ln [\pi / (\sigma^2 I_a I_b I_c)], \quad (6)$$

where  $\sigma$  is the rotational symmetry parameter and  $I_a I_b I_c$  is the product of the three moments of inertia. These are related to the rotational constants by

$$I_b = h/8\pi^2 B, \quad (7)$$

where  $B$  is the rotational constant.

The vibrational contribution for each fundamental vibrational mode is

$$S_{vi}^0/R = u_i e^{-u_i} / (1 - e^{-u_i}) - \ln(1 - e^{-u_i}). \quad (8)$$



The total entropy is the sum of  $S_{vi}^0$  for each fundamental vibrational mode plus  $S_r^0$  and  $S^0$  as given in Eqs. (5), (6), and (8).

### 3.1.4. Gibbs Energy Function

The temperature dependence of the Gibbs energy function is

$$\begin{aligned} & [G^0(T) - H^0(298.15)]/T \\ & = -S^0(T) + [H^0(T) - H^0(298.15)]/T. \end{aligned} \quad (9)$$

### 3.1.5. Enthalpy of Formation

The temperature dependence for the enthalpy for formation requires the value of the enthalpy of formation at one temperature, the enthalpy for the compound [Eq. (4)] and the enthalpy for the elements

$$\begin{aligned} \Delta_f H^0(T) &= \Delta_f H^0(298.15) + [H^0(T) - H^0(298.15)]_{\text{compound}} \\ & - \sum [H^0(T) - H^0(298.15)]_{\text{elements}}. \end{aligned} \quad (10)$$

### 3.1.6. Gibbs Energy of Formation

The Gibbs energy of formation is

$$\Delta G^0(T) = \Delta_f H^0(T) - T[S^0(T)_{\text{compound}} - \Delta S^0(T)_{\text{elements}}]. \quad (11)$$

The enthalpy and entropy information for the elements Si and F is available in the NIST-JANAF Thermochemical Tables.<sup>25</sup>

### 3.1.7. Equilibrium Constant

The parameter  $-\log K_{\text{eq}}$  is the negative logarithm of the equilibrium constant for formation of the species from its elements in their standard state. It is just

$$-\log K_{\text{eq}} = \Delta_f G^0(T)/RT. \quad (12)$$

### 3.1.8. Hindered Rotation

We also find it necessary to account for the effect of the hindered rotation about the Si-Si bond in Si<sub>2</sub>F<sub>6</sub>. The procedure we used is that suggested by McClurg, *et al.*<sup>39</sup> It formulates an approximate partition function that fits the exact calculation well for either a low or high rotational barrier. The single parameter necessary for calculation of the effect of hindered rotation is  $r$ , the ratio of the rotational barrier height to the harmonic oscillator frequency of the vibrational mode that becomes the hindered rotation. The correction to the heat capacity for that mode is

$$\Delta C_v/R = -1/2 + z^2/2 \{1 - 2[I_1(z)/I_0(z)]^2 + I_2(z)/I_0(z)\}, \quad (13)$$

where

$$z = r/2\Theta, \quad (14)$$

and

$$\Theta = kT/h\nu = T/(c_2 \cdot \nu_h). \quad (15)$$

The frequency  $\nu_h$  is that of the vibrational mode that becomes the hindered rotation. The Mathieu functions<sup>40</sup> in Eq. (13) are

$$I_\nu(x) = \sum_{k=0}^{\infty} (x/2)^{\nu+2k}/(k!(k+\nu)!) \quad \text{for } x < 3.75 \quad (16)$$

and

$$\begin{aligned} I_\nu(x) &= \exp(x)/(2\pi x)^{1/2} \sum_{k=0}^{\infty} ((-1)^k \Gamma(\nu+k+1/2)) / \\ & (2x)^k k! \Gamma(\nu-k+1/2) \end{aligned} \quad (17)$$

for  $x > 3.75$ . A correction similar to Eq. (13) for the enthalpy is

$$\begin{aligned} \Delta[H^0(T) - H^0(298.15)]/RT \\ & = -1/2 - 1/(2+16r)/\Theta + z\{1 - I_1[z]/I_0[z]\}. \end{aligned} \quad (18)$$

(We note that the enthalpy expression is not correct in the original reference.<sup>39</sup> It is correct here.<sup>41</sup>) The entropy correction is

$$\begin{aligned} \Delta S/R &= -1/2 + z\{1 + I_1[z]/I_0[z]\} - z \\ & + \ln[(2\pi z)^{0.5} I_0(z)]. \end{aligned} \quad (19)$$

The physical constants necessary for calculation of the thermochemical functions of ideal gas polyatomic molecules in the harmonic oscillator approximation are listed in Sec. 1.

## 3.2. Thermochemical Functions in CHEMKIN Format

For modeling applications, the thermochemical functions are often expressed in polynomial form for use in applications such as CHEMKIN. The approach<sup>23</sup> for obtaining these constants is first to fit the heat capacity to the following five-parameter polynomial

$$C_p/R = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4. \quad (20)$$

We then solve the enthalpy equation

$$H^0/R = a_1 + a_2/2T + a_3/3T^2 + a_4/4T^3 + a_5/5T^4 + a_6/T \quad (21)$$

for the constant  $a_6$  with the added information of the value of  $\Delta_f H^0(298.15)$ . Finally, we solve the entropy equation

$$S^0/R = a_1 \ln T + a_2 T + a_3/2T^2 + a_4/3T^3 + a_5/4T^4 + a_7 \quad (22)$$

for the constant  $a_7$  with the added information of the value of  $S^0(298.15)$ . It is best to obtain the set of constants for both low and high temperature ranges. The common temperature is most often 1000 K. We use that temperature for the values presented in this paper.

### 3.3. Thermochemical Functions Corrected for Anharmonicity

Few molecules have had sufficiently complete infrared analysis to determine the effect of the harmonic oscillator approximation on the thermochemical functions of a polyatomic molecule. McDowell, *et al.*<sup>13</sup> have made the necessary analysis to allow making the evaluation for  $\text{SiF}_4$ . We may not use Eqs. (2)–(12) to calculate the effect of molecular anharmonicity on the thermochemical functions. Those equations are based on statistical mechanical partition functions, which follow directly from the harmonic oscillator approximation. We can, however, obtain the vibrational part of the partition function, and hence the thermochemical functions, from a direct count of vibrational states. The vibrational part of the partition function is just

$$q_v = \sum_{k=1}^{\infty} g_k \exp(-E_k/kT). \quad (23)$$

The sum is over all vibrational states of the molecule. One can calculate the energies of those states  $E_k$  from the fundamental vibrational frequencies  $\nu_i$  and the anharmonicity constants  $X_{ij}$ . The vibrational energy<sup>13</sup> of state  $k$ , correct to second order, is

$$E_k = \sum_{i=1}^n \omega_i + \sum_{i=1}^n X_{ii} \nu_i (\nu_i + d_i) (1/2) \\ \times \sum_{i=1}^n \sum_{j \neq i}^n X_{ij} \nu_i (\nu_j + d_j) + W', \quad (24)$$

where  $n$  is the number of vibrational modes of the molecule,  $\nu_i$  is the vibrational quantum number of vibrational mode  $i$ ,  $d_i$  is the degeneracy of vibrational mode  $i$ ,  $\omega_i$  is the vibrational frequency, and  $W'$  is all of the second order shifts and splittings of the state. We ignore  $W'$  for this calculation. The effective harmonic vibrational frequency,  $\omega_i^0$ , for mode  $i$  is related to this set of constants by

$$\omega_i^0 = \omega_i + X_{ii} d_i + (1/2) \sum_{j \neq i}^n X_{ij} d_j. \quad (25)$$

The constant  $n=4$  is the number of vibrational modes. This is the frequency of the transition from  $\nu_i=0$  to  $\nu_i=1$  with  $\nu_j=0$  for  $j \neq i$ . It is the observed vibrational frequency used in the calculations for the harmonic oscillator approximation. Using Eq. (25) and neglecting  $W'$  simplifies Eq. (24) as

$$E_k = \sum_{i=1}^n \omega_i^0 \nu_i + \sum_{i < j}^n X_{ij} \nu_i \nu_j, \quad (26)$$

where  $n$  is the number of vibrational modes. We use Eq. (26) to obtain the state energies for the vibrational partition function [Eq. (23)]. The state degeneracies,  $g_k$ , in Eq. (23) are simple functions of the mode degeneracies  $d_j$  and the vibrational quantum numbers  $\nu_j$  in Eq. (24)

$$g_k = \prod_{i=1}^n \{(\nu_i + d_i - 1)! / [\nu_i! (d_i - 1)!\}]. \quad (27)$$

In this expression “ $i$ ” indexes the  $n$  (four) vibrational quantum numbers. The degeneracy of state  $k$  is then the product of four factors that follow from the vibrational quantum numbers and the mode degeneracies. Calculation of  $q_v$  [Eq. (23)] requires counting all of the vibrational states by considering all combinations of the four quantum numbers. The number of states counted is up to the energy where the states have no more significance at the highest temperatures considered. We performed this count for all vibrational states up to a total vibrational energy of  $100\,000 \text{ cm}^{-1}$ .

## 4. Thermochemical Parameters for $\text{Si}_2\text{F}_6$

### 4.1. Thermochemical Parameters for $\text{Si}_2\text{F}_6$ (Ideal Gas)

#### 4.1.1. Parameters in NIST–JANAF Thermochemical Tables Format

Given the above expressions [Eqs. (2)–(19)] and the molecular properties called for in those equations (Table 1), the thermochemical parameters for  $\text{Si}_2\text{F}_6$  ideal gas are calculated. The results are given in Table 2 the format of the NIST–JANAF Thermochemical Tables.<sup>25</sup> The calculations include the effect of the hindered rotation about the Si–Si bond. Figure 1 shows that the hindered rotation effects the heat capacity most at high temperature. The limiting correction at high temperature is  $-1/2 R$ . The hindered rotation increases the heat capacity [Eq. (13)] at low temperature and decreases the heat capacity at high temperature. It has a similar effect on the enthalpy and entropy functions [Eqs. (18) and (19)].

#### 4.1.2. Parameters in CHEMKIN Format

Table 3 gives the constants that produce the thermochemical parameters for  $\text{Si}_2\text{F}_6$  (ideal gas) in the format of the CHEMKIN parameters, Eqs. (20)–(22).

To see how these calculations compare with the thermochemical parameters given in the earlier version<sup>23</sup> of the CHEMKIN parameters we plot both the heat capacity and the entropy for the molecule. Figure 1 shows the comparison of the heat capacity and Fig. 2 shows a comparison of the entropy. We note that the values of the heat capacity are nearly identical, but the CHEMKIN values are higher by a small amount. It appears (Fig. 1) that the CHEMKIN formulas included the hindered rotation effect because the heat capacity is correct in the high temperature limit. The CHEMKIN values for entropy (Fig. 2) are also higher over the same temperature range.

TABLE 1. Parameters for calculation of the thermochemical properties for Si<sub>2</sub>F<sub>6</sub> (ideal gas)

Parameter	Symbol	Value	<i>d</i> <sup>a</sup>	Reference
Molecular weight	<i>M<sub>r</sub></i>	170.161	—	31
Rotational constants	<i>A</i>	0.06875	—	21
	<i>B</i> <sup>b</sup>	0.03194	—	21
Vibrational frequencies/cm <sup>-1</sup>	<i>ν</i> <sub>1</sub>	915	1	21
	<i>ν</i> <sub>2</sub>	545	1	21
	<i>ν</i> <sub>3</sub>	218	1	21
	<i>ν</i> <sub>4</sub>	38	1	21
	<i>ν</i> <sub>5</sub>	823.6	1	21
	<i>ν</i> <sub>6</sub>	406	1	21
	<i>ν</i> <sub>7</sub>	991.6	2	21
	<i>ν</i> <sub>8</sub>	310	2	21
	<i>ν</i> <sub>9</sub>	103	2	21
	<i>ν</i> <sub>10</sub>	979	2	21
	<i>ν</i> <sub>11</sub>	340	2	21
	<i>ν</i> <sub>12</sub>	203	2	21
Barrier for internal rotation	<i>W</i>	530 ± 20 <sup>c</sup>	—	21
Enthalpy of formation, 298.15 K	Δ <sub><i>f</i></sub> <i>H</i> <sup>0</sup>	-569.62 ± 3.47 <sup>d</sup>	—	17
Symmetry parameter	σ	6	—	17

<sup>a</sup>Degeneracy of the vibrational modes.

<sup>b</sup>The molecule is a symmetric top, the rotational constant *C* = *B*.

<sup>c</sup>cm<sup>-1</sup>.

<sup>d</sup>kcal/mol. The value in Pedley and Iseard<sup>18</sup> is -565.56 ± 8.17 kcal/mol and McClurg<sup>41</sup> gives an upper limit of -558.56 kcal/mol. Both are consistent with the value in the table.

We can trace the difference between our parameters and those of CHEMKIN to differences in the vibrational frequencies. As we noted above the CHEMKIN source is the calculations of Ho and Melius.<sup>17</sup> An individual comparison of each of the experimental vibrational frequencies in Table 1 (from Tosa *et al.*<sup>21</sup>) with the calculated vibrational frequencies of Ho and Melius<sup>17</sup> indicates that each of the experimental frequencies exceeds the corresponding calculated frequency. The average experimental frequency<sup>21</sup> is 4.6% greater than the corresponding calculated value.<sup>17</sup> The largest deviation is for the lowest frequency. The lowest experimental frequency (38 cm<sup>-1</sup>) is 60% greater than the lowest calculated frequency.

## 4.2. Thermochemical Parameters for Si<sub>2</sub>F<sub>6</sub> (Solid)

### 4.2.1. Vapor Pressure of Si<sub>2</sub>F<sub>6</sub>

The vapor pressure over solid Si<sub>2</sub>F<sub>6</sub> has been reported by Stull.<sup>29</sup> Figure 3 shows the vapor pressure over the temperature range of the experiments of Stull.<sup>29</sup> The enthalpy and entropy changes for sublimation follow directly from those measurements using the Clapeyron–Clausius<sup>38</sup> equation

$$\Delta S_s = 171.878 \text{ J/K/mol} \quad (28)$$

and

$$\Delta H_s = 43.674 \text{ kJ/mol.} \quad (29)$$

### 4.2.2. Parameters for Si<sub>2</sub>F<sub>6</sub> (Solid)

Using the values given in Eqs. (28) and (29) with the Si<sub>2</sub>F<sub>6</sub> (ideal gas) thermochemical parameters in Table 2, the entropy, enthalpy of formation, and Gibbs energy function for Si<sub>2</sub>F<sub>6</sub> (solid) are calculated. The heat capacity for Si<sub>2</sub>F<sub>6</sub> (solid) follows directly from the temperature derivative of the enthalpy function (*H*<sup>0</sup>(*T*) - *H*<sup>0</sup>(*T<sub>r</sub>*)). Table 4 shows these four functions from *T*/K = 0 to *T*/K = 1500.

The boiling point<sup>29</sup> for solid Si<sub>2</sub>F<sub>6</sub> at a pressure of 1 bar is 254.3 K, which is below the melting point, 254.6 K. Thus, no data are presented for liquid Si<sub>2</sub>F<sub>6</sub>.

## 5. Thermochemical Parameters for SiF<sub>4</sub>

### 5.1. Thermochemical Parameters for SiF<sub>4</sub> (Ideal Gas)

#### 5.1.1. Parameters in the NIST–JANAF Thermochemical Tables Format

As we noted above, the thermochemistry of SiF<sub>4</sub> is quite well known. Newer spectroscopic measurements<sup>13</sup> were not available at the date of the SiF<sub>4</sub> entry in the NIST–JANAF Thermochemical Tables.<sup>25</sup> The enthalpy of formation, determined by Johnson,<sup>1</sup> and given in Eq. (1) is used in these calculations. The parameters for each isotopomer are calculated and then averaged over the natural isotope distribution for the three silicon isotopes. Table 5 shows the parameters used for calculating the thermochemical parameters. The results for SiF<sub>4</sub>, as an ideal gas using the harmonic oscillator

TABLE 2. Thermochemical properties of disilicon hexafluoride (ideal gas) (enthalpy reference temperature =  $T_r = 298.15$  K, standard state pressure =  $p^0 = 0.1$  MPa)

T/K	J K <sup>-1</sup> mol <sup>-1</sup>			kJ mol <sup>-1</sup>			log $K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
0	0.000	0.000	infinite	-26.682	-2377.061	-2377.061	Infinite
100	76.707	278.148	492.223	-21.408	-2381.040	-2356.977	1231.142
200	110.468	343.014	402.288	-11.855	-2382.632	-2332.178	609.094
225	116.144	356.364	396.459	-9.021	-2382.873	-2325.954	539.972
250	121.262	368.866	393.075	-6.052	-2383.053	-2319.592	484.646
275	125.921	380.644	391.412	-2.961	-2383.191	-2313.180	439.369
298.15	129.877	390.983	390.983	0.000	-2383.290	-2307.255	404.216
300	130.180	391.787	390.986	0.241	-2383.298	-2306.783	401.641
325	134.073	402.364	391.459	3.544	-2383.378	-2300.434	369.725
350	137.627	412.431	392.599	6.941	-2383.434	-2294.119	342.374
375	140.863	422.037	394.240	10.424	-2383.462	-2287.769	318.665
400	143.805	431.225	396.270	13.982	-2383.457	-2281.242	297.896
450	148.898	448.467	401.125	21.304	-2383.384	-2268.566	263.325
500	153.087	464.379	406.665	28.857	-2383.234	-2255.707	235.649
600	159.395	492.884	418.716	44.501	-2382.761	-2230.241	194.157
700	163.759	517.802	431.129	60.671	-2382.143	-2204.869	164.527
800	166.857	539.883	443.369	77.211	-2381.448	-2179.589	142.311
900	169.116	559.673	455.212	94.015	-2380.731	-2154.402	125.037
1000	170.805	577.583	466.567	111.015	-2380.025	-2129.294	111.221
1100	172.095	593.925	477.413	128.163	-2379.346	-2104.252	99.921
1200	173.100	608.944	487.757	145.424	-2378.721	-2079.273	90.507
1300	173.897	622.832	497.620	162.776	-2378.159	-2054.344	82.543
1400	174.539	635.744	507.030	180.199	-2377.672	-2029.453	75.719
1500	175.064	647.804	516.018	197.680	-2377.272	-2004.596	69.805
1600	175.497	659.117	524.611	215.208	-2376.963	-1979.761	64.632
1700	175.859	669.767	532.840	232.777	-2477.099	-1954.047	60.040
1800	176.164	679.828	540.729	250.378	-2476.518	-1923.300	55.812
1900	176.424	689.360	548.303	268.008	-2476.554	-1893.191	52.047
2000	176.647	698.415	555.584	285.662	-2475.371	-1861.889	48.627
2100	176.840	707.038	562.592	303.337	-2474.796	-1831.231	45.549
2200	177.008	715.269	569.347	321.029	-2474.210	-1800.596	42.751
2300	177.154	723.141	575.864	338.737	-2473.606	-1769.991	40.197
2400	177.283	730.683	582.158	356.459	-2472.974	-1739.409	37.857
2500	177.398	737.922	588.245	374.194	-2472.302	-1708.863	35.704
2600	177.499	744.882	594.137	391.938	-2471.584	-1678.337	33.718
2700	177.590	751.583	599.845	409.693	-2470.807	-1647.841	31.879
2800	177.671	758.043	605.380	427.456	-2469.968	-1617.378	30.172
2900	177.744	764.279	610.752	445.227	-2469.050	-1586.948	28.584
3000	177.810	770.306	615.971	463.005	-2468.055	-1556.546	27.102
3100	177.870	776.137	621.044	480.789	-2466.974	-1526.180	25.716
3200	177.924	781.785	625.979	498.578	-2465.803	-1495.848	24.417
3300	177.974	787.261	630.784	516.373	-2464.536	-1465.549	23.197
3400	178.019	792.575	635.465	534.173	-2463.166	-1435.311	22.051
3500	178.060	797.735	640.028	551.977	-2461.700	-1405.097	20.970
3600	178.098	802.752	644.479	569.785	-3228.424	-1354.005	19.646
3700	178.133	807.632	648.822	587.597	-3225.919	-1301.968	18.380
3800	178.166	812.383	653.064	605.412	-3223.312	-1250.008	17.182
3900	178.196	817.012	657.209	623.230	-3220.601	-1198.110	16.047
4000	178.223	821.523	661.261	641.051	-3217.786	-1146.292	14.969
4100	178.249	825.925	665.224	658.874	-3214.871	-1094.534	13.944
4200	178.273	830.220	669.101	676.700	-3211.849	-1042.861	12.970



TABLE 2. Thermochemical properties of disilicon hexafluoride (ideal gas) (enthalpy reference temperature= $T_r=298.15$  K, standard state pressure= $p^0=0.1$  MPa)—Continued

$T/\text{K}$	$\text{J K}^{-1} \text{mol}^{-1}$			$\text{kJ mol}^{-1}$			$\log K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
4300	178.295	834.415	672.897	694.529	-3208.730	-991.256	12.041
4400	178.316	838.515	676.615	712.359	-3205.508	-939.722	11.156
4500	178.336	842.522	680.257	730.192	-3202.186	-888.264	10.311
4600	178.354	846.442	683.827	748.026	-3198.768	-836.888	9.503
4700	178.371	850.278	687.328	765.863	-3195.255	-785.573	8.731
4800	178.387	854.033	690.762	783.701	-3191.652	-734.341	7.991
4900	178.402	857.712	694.132	801.540	-3187.954	-683.194	7.283
5000	178.416	861.316	697.440	819.381	-3184.169	-632.104	6.603
5100	178.429	864.849	700.688	837.223	-3180.302	-581.113	5.952
5200	178.442	868.314	703.878	855.067	-3176.349	-530.168	5.326
5300	178.454	871.713	707.013	872.911	-3172.316	-479.340	4.724
5400	178.465	875.049	710.094	890.757	-3168.205	-428.547	4.145
5500	178.475	878.324	713.123	908.604	-3164.017	-377.859	3.589
5600	178.485	881.540	716.102	926.452	-3159.760	-327.239	3.052
5700	178.495	884.699	719.032	944.301	-3155.431	-276.696	2.536
5800	178.504	887.803	721.915	962.151	-3151.036	-226.213	2.037
5900	178.513	890.855	724.753	980.002	-3146.572	-175.850	1.557
6000	178.521	893.855	727.546	997.854	-3142.050	-125.527	1.093

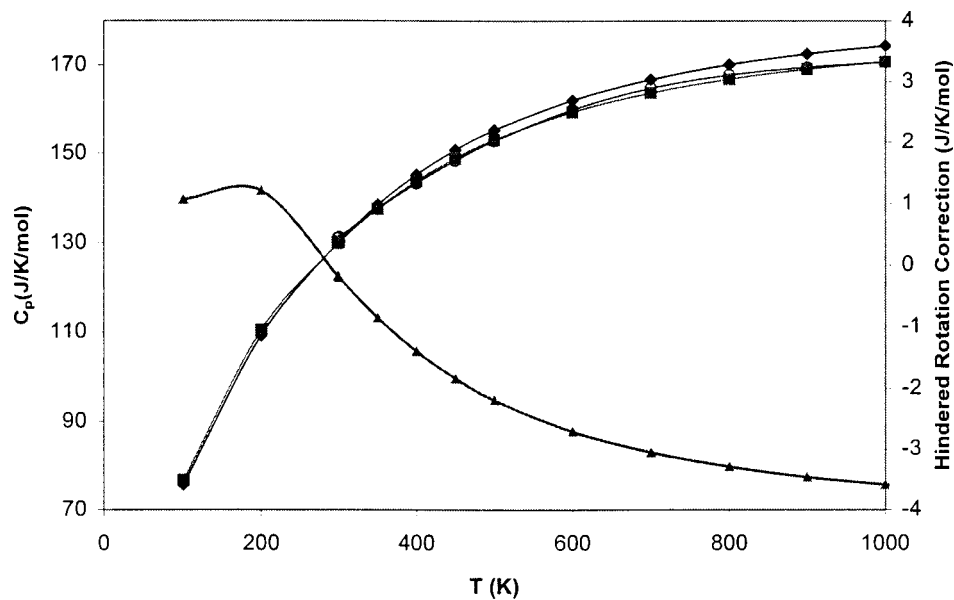


FIG. 1. Heat capacity of  $\text{Si}_2\text{F}_6$  ideal gas up to 1000 K. The solid diamonds are the calculation of  $C_p$  without the hindered rotation correction. The solid squares (Table 2) are with the correction. The open circles are calculated from the CHEMKin constants.<sup>23</sup> The solid triangles are the hindered rotation correction, right axis.

TABLE 3.  $\text{Si}_2\text{F}_6$  (ideal gas) coefficients, CHEMKin format

	Low (100–1000 K)	High (1000–5000 K)
$a_1$	5.52450090E+00	1.84343713E+01
$a_2$	5.19161565E-02	3.31723030E-03
$a_3$	-7.49444734E-05	-1.41645424E-06
$a_4$	5.26341581E-08	2.69792894E-10
$a_5$	-1.45880530E-11	-1.90290332E-14
$a_6$	-2.90035364E+05	-2.92978079E+05
$a_7$	2.96443224E+00	-6.05666535E+01

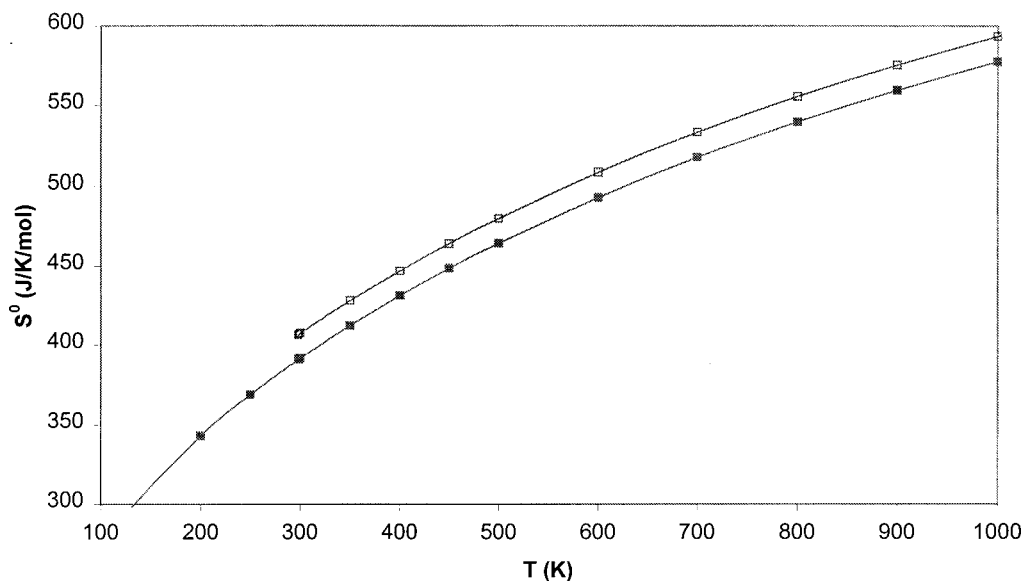


FIG. 2. Entropy of  $\text{Si}_2\text{F}_6$  ideal gas up to 1000 K. Solid squares indicate our calculation of the entropy (Table 2), and the open squares are from the CHEMKin constants of Lee *et al.*<sup>23</sup>

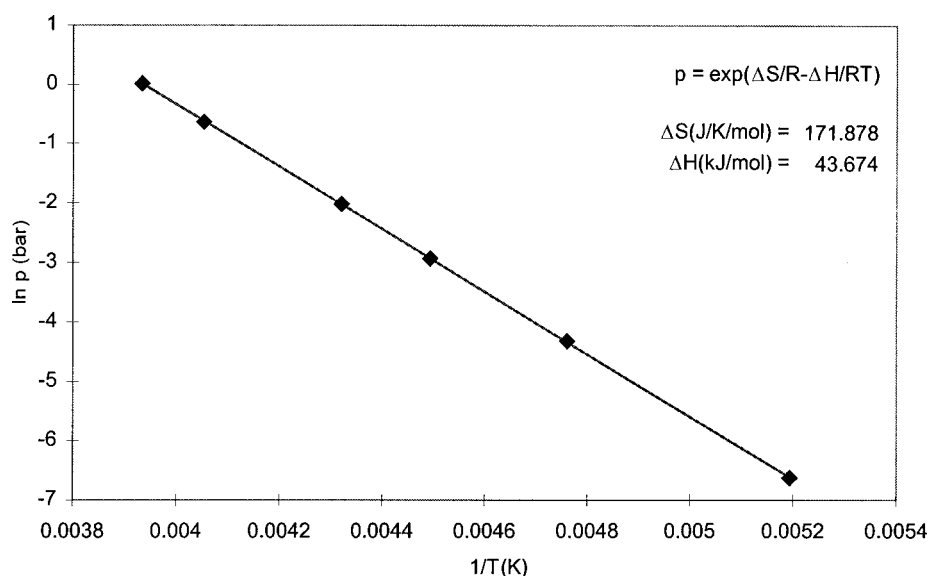


FIG. 3. Sublimation pressure<sup>29</sup> of  $\text{Si}_2\text{F}_6$ .

approximation [Eqs. (2)–(12)], are given in Table 6 in the format of the NIST–JANAF Thermochemical Tables.<sup>25</sup> The values in Table 6 are very close to those in an earlier publication.<sup>25</sup> The vibrational frequencies used in each calculation differ slightly. The experimental values used in this calculation are given in Table 5. The average frequency in

TABLE 4. Thermochemical properties of disilicon hexafluoride (solid) (enthalpy reference temperature =  $T_r = 298.15$  K, standard state pressure =  $p^0 = 0.1$  MPa)

$T/\text{K}$	$\text{J K}^{-1} \text{mol}^{-1}$		$\text{kJ mol}^{-1}$	
	$C_p^0$	$S^0$	$\Delta_f H^0$	$\Delta_f G^0$
0	0.000	0.000	-2420.735	-2420.735
100	82.718	106.271	-2424.713	-2383.463
200	109.750	171.137	-2426.306	-2341.476
225	115.370	184.486	-2426.547	-2330.955
250	120.572	196.988	-2426.727	-2320.297
254.1	121.366	198.685	-2426.739	-2318.876
275	125.373	208.766	-2426.865	-2309.587
298.15	129.453	219.105	-2426.964	-2299.683
300	129.793	219.910	-2426.971	-2298.894
325	133.849	230.487	-2427.052	-2288.247
350	137.561	240.554	-2427.108	-2277.636
375	140.945	250.159	-2427.136	-2266.989
400	144.021	259.348	-2427.131	-2256.165
450	149.321	276.589	-2427.058	-2234.895
500	153.608	292.501	-2426.908	-2213.442
600	159.726	321.006	-2426.435	-2170.788
700	163.549	345.924	-2425.817	-2128.229
800	166.252	368.005	-2425.122	-2085.761
900	169.007	387.795	-2424.405	-2043.385
1000	172.988	405.705	-2423.699	-2001.090
1100	179.369	422.047	-2423.020	-1958.860
1200	189.323	437.066	-2422.394	-1916.693
1300	204.024	450.954	-2421.833	-1874.576
1400	224.645	463.866	-2421.346	-1832.498
1500	252.359	475.926	-2420.946	-1790.453

that table is lower than the frequencies used in the NIST–JANAF Thermochemical Tables<sup>25</sup> by  $0.6 \text{ cm}^{-1}$ . This results in a small increase in most of the thermochemical parameters. Figure 4 shows the difference between the parameters in Table 6 and those in the NIST–JANAF Thermochemical Tables.<sup>25</sup> The figure shows the difference for heat capacity, entropy, and Gibbs energy function temperature dependence; each of which has units of  $\text{J/K/mol}$ . For all three functions and all temperatures the difference is in the range of  $-0.1$ – $0.2 \text{ J/K/mol}$ . We have attempted to determine the reason for the higher values for the entropy difference and for the Gibbs energy function temperature dependence in Fig. 4. The differences are about what one would expect if the authors of the NIST–JANAF Thermochemical Tables used a standard state pressure of 1 atm instead of 0.1 MPa. The 0.1 MPa standard state pressure would increase the entropy about  $0.11 \text{ J/K/mol}$  [see Eq. (5)]. The additional difference can be accounted for by the minor differences in vibrational frequencies and averaging the parameters for the three isotopes.

Figure 5 shows the difference for the functions with units of  $\text{kJ/mol}$ , the enthalpy [ $H - H(T_r)$ ], the enthalpy of formation, and the Gibbs energy of formation. The enthalpy and the enthalpy of formation differences are both similar in magnitude to those of the heat capacity (Fig. 4) if expressed in similar units by dividing by temperature. These differences reflect the small spread in the fundamental vibrational frequencies. The trend with temperature for the Gibbs energy of formation follows from the difference we saw in the entropy function (Fig. 4).

### 5.1.2. Parameters in CHEMKIN Format

Table 6 was also used to derive the coefficients in the format of the CHEMKIN thermochemistry databases for

TABLE 5. Parameters for calculation of the thermochemical properties for SiF<sub>4</sub> (ideal gas)

Parameter	Symbol	Value	<i>d</i> <sup>a</sup>	Reference
Molecular weight	$M_r$ ( $M_r$ <sup>32</sup> SiF <sub>4</sub> = 103.8913) ( $M_r$ <sup>33</sup> SiF <sub>4</sub> = 104.8913) ( $M_r$ <sup>34</sup> SiF <sub>4</sub> = 105.8913)	104.0791 <sup>b</sup>	—	31
Rotational constant	$B^c$	0.13814 <sup>d</sup>	—	25
Vibrational frequencies	$\nu_1$	800.6 <sup>d</sup>	1	13
	$\nu_2$	264.2 <sup>d</sup>	2	13
	<sup>32</sup> SiF <sub>4</sub> $\nu_3$	1027.977 <sup>d</sup>	3	13
	<sup>33</sup> SiF <sub>4</sub> <sup>34</sup> SiF <sub>4</sub>	1018.997 <sup>d</sup> 1010.577 <sup>d</sup>		
<sup>32</sup> SiF <sub>4</sub>	$\nu_4$	388.50 <sup>d</sup>	3	13
<sup>33</sup> SiF <sub>4</sub>		386.95 <sup>d</sup>		
<sup>34</sup> SiF <sub>4</sub>		385.50 <sup>d</sup>		
Enthalpy of formation, 298.15 K	$\Delta_f H^0$	-386.18 ± 0.11 <sup>e</sup>	—	14
Symmetry parameter	$\sigma$	12	—	25

<sup>a</sup>Degeneracy of the vibrational modes.<sup>b</sup>g/mol.<sup>c</sup>The molecule is a spherical top, and the rotational constants are all equal.<sup>d</sup>cm<sup>-1</sup>.<sup>e</sup>kcal/mol.

SiF<sub>4</sub> (ideal gas). The results are given in Table 7 for the two temperature regions above and below 1000 K. These constants differ by a small amount from those in the earlier CHEMKIN thermochemical database.<sup>23</sup>

## 5.2. Thermochemical Parameters for SiF<sub>4</sub> in Condensed Phases

### 5.2.1. Vapor Pressure of SiF<sub>4</sub>

The vapor pressure of SiF<sub>4</sub>, the sources of which were discussed above, provide a connection between the ideal gas thermochemical parameters and those of the condensed phases. Figure 6 shows the vapor pressure measurements for both solid and liquid SiF<sub>4</sub>. The recommended values of Kalish and Tabachnikov,<sup>32</sup> which is the solid line in Fig. 6, are used. This gives values of the entropy and enthalpy of sublimation just below the critical point, 186.35 K, and the entropy and enthalpy of vaporization just above the critical point. This, along with some additional phase change information, is given in Table 8. The entropy and enthalpy changes are sufficiently precise to give some temperature dependence away from the critical point.

### 5.2.2. Parameters for Condensed Phases in NIST-JANAF Thermochemical Tables Format

With that dependence and the ideal gas thermochemical parameters of Table 6, the entropy and enthalpy of formation for SiF<sub>4</sub> in the two condensed phases at low temperatures can be obtained. Furthermore, with independent measurements of the heat capacity for both solid<sup>15</sup> SiF<sub>4</sub> and liquid<sup>16</sup> SiF<sub>4</sub>, a full thermochemical table can be constructed. Figure 7 shows the heat capacity results from those two sources. Table 9

gives the thermochemical parameters at selected temperatures for SiF<sub>4</sub> (solid) and Table 10 gives the parameters for SiF<sub>4</sub> (liquid).

To show the differences among the three phases of SiF<sub>4</sub>, the enthalpies of formation for the three phases in the temperature range below 400 K are shown in Fig. 8.

## 5.3. Thermochemical Parameters for Anharmonic SiF<sub>4</sub> (Ideal Gas)

The effect of the measured<sup>13</sup> anharmonicity for SiF<sub>4</sub> is calculated by counting the vibrational states and determining both the energy and degeneracy of each state. Equation (26) gives the energy and Eq. (27) the degeneracy of each of the *k* states counted. Equation (23) gives the vibrational partition function. It is assumed that the translational and rotational contributions to the partition function are unchanged by the molecular anharmonicity. Table 11 shows the anharmonicity parameters<sup>13</sup> used in the calculations. The values of Wang *et al.*<sup>27</sup> are similar. Only their value for *X*<sub>14</sub> (0.109 cm<sup>-1</sup>) differs significantly from those in Table 11. Again, as for Table 6, the values obtained for the anharmonic assumption are an average over the natural distribution of silicon isotopes.

A direct count of the vibrational states up to an energy of 100 000 cm<sup>-1</sup> was made. Figure 9 shows the density of vibrational states for both the harmonic and anharmonic assumptions between 10 000 and 100 000 cm<sup>-1</sup>. We note that the density-of-states lines are about equal near 18 000 cm<sup>-1</sup>, but they spread to where they differ by about a factor of 2 at the high energies. The zero values for *X*<sub>22</sub> and for *X*<sub>24</sub> and the positive value for *X*<sub>14</sub> are sufficient to make the anharmonic density of states at low energies lower than that of the

TABLE 6. Thermochemical properties of silicon tetrafluoride (ideal gas, harmonic oscillator) (enthalpy reference temperature= $T_r=298.15$  K, standard state pressure= $p^0=0.1$  MPa)

$T/\text{K}$	$\text{J K}^{-1} \text{mol}^{-1}$			$\text{kJ mol}^{-1}$			$\log K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
0	0.000	0.000	infinite	-15.361	-1610.273	-1610.273	infinite
100	41.826	220.789	339.175	-11.839	-1612.831	-1600.452	835.979
200	60.905	256.074	289.260	-6.637	-1614.666	-1587.287	414.551
225	64.557	263.461	285.987	-5.068	-1615.011	-1583.897	367.703
250	67.910	270.439	284.087	-3.412	-1615.307	-1580.411	330.204
275	71.007	277.059	283.149	-1.675	-1615.566	-1576.876	299.514
298.15	73.666	282.905	282.905	0.000	-1615.780	-1573.594	275.683
300	73.870	283.361	282.907	0.136	-1615.797	-1573.332	273.938
325	76.509	289.380	283.175	2.017	-1616.002	-1569.799	252.298
350	78.936	295.140	283.825	3.960	-1616.186	-1566.273	233.750
375	81.160	300.663	284.765	5.962	-1616.345	-1562.719	217.672
400	83.193	305.967	285.925	8.017	-1616.476	-1559.064	203.590
450	86.735	315.976	288.715	12.268	-1616.683	-1551.923	180.140
500	89.672	325.272	291.912	16.680	-1616.822	-1544.665	161.368
600	94.130	342.040	298.900	25.884	-1616.940	-1530.219	133.216
700	97.240	356.798	306.139	35.461	-1616.915	-1515.766	113.106
800	99.461	369.935	313.307	45.302	-1616.801	-1501.322	98.025
900	101.087	381.749	320.267	55.334	-1616.640	-1486.898	86.296
1000	102.305	392.465	326.959	65.506	-1616.460	-1472.492	76.914
1100	103.238	402.262	333.366	75.785	-1616.275	-1458.103	69.239
1200	103.967	411.277	339.488	86.147	-1616.104	-1443.732	62.843
1300	104.545	419.623	345.335	96.574	-1615.957	-1429.375	57.432
1400	105.011	427.388	350.922	107.052	-1615.842	-1415.027	52.795
1500	105.392	434.646	356.264	117.573	-1615.767	-1400.687	48.776
1600	105.708	441.459	361.378	128.129	-1615.735	-1386.349	45.259
1700	105.971	447.875	366.279	138.713	-1665.926	-1371.564	42.142
1800	106.193	453.939	370.982	149.322	-1665.757	-1354.256	39.299
1900	106.383	459.686	375.501	159.951	-1665.897	-1337.259	36.763
2000	106.545	465.147	379.848	170.597	-1665.427	-1319.660	34.466
2100	106.686	470.348	384.035	181.259	-1665.258	-1302.377	32.394
2200	106.808	475.314	388.072	191.934	-1665.081	-1285.100	30.512
2300	106.915	480.064	391.969	202.620	-1664.891	-1267.832	28.793
2400	107.009	484.617	395.735	213.316	-1664.682	-1250.571	27.218
2500	107.093	488.987	399.378	224.022	-1664.444	-1233.324	25.769
2600	107.167	493.189	402.906	234.735	-1664.176	-1216.083	24.431
2700	107.233	497.234	406.325	245.455	-1663.868	-1198.854	23.193
2800	107.292	501.135	409.642	256.181	-1663.518	-1181.639	22.043
2900	107.345	504.901	412.862	266.913	-1663.115	-1164.437	20.974
3000	107.393	508.541	415.991	277.650	-1662.660	-1147.249	19.975
3100	107.437	512.063	419.034	288.391	-1662.148	-1130.077	19.041
3200	107.477	515.475	421.995	299.137	-1661.574	-1112.921	18.166
3300	107.513	518.783	424.878	309.887	-1660.936	-1095.781	17.345
3400	107.546	521.993	427.687	320.640	-1660.230	-1078.673	16.572
3500	107.576	525.111	430.426	331.396	-1659.459	-1061.578	15.843
3600	107.604	528.142	433.099	342.155	-2042.765	-1034.044	15.003
3700	107.630	531.090	435.707	352.916	-2041.439	-1006.040	14.203
3800	107.653	533.961	438.255	363.681	-2040.045	-978.077	13.444
3900	107.675	536.757	440.745	374.447	-2038.580	-950.146	12.726
4000	107.695	539.484	443.180	385.216	-2037.045	-922.261	12.043
4100	107.714	542.143	445.561	395.986	-2035.444	-894.407	11.395
4200	107.732	544.739	447.892	406.758	-2033.770	-866.600	10.778



TABLE 6. Thermochemical properties of silicon tetrafluoride (ideal gas, harmonic oscillator) (enthalpy reference temperature= $T_r=298.15$  K, standard state pressure= $p^0=0.1$  MPa)—Continued

$T/K$	$\text{J K}^{-1} \text{mol}^{-1}$			$\text{kJ mol}^{-1}$			$\log K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
4300	107.748	547.274	450.174	417.532	-2032.032	-838.831	10.190
4400	107.763	549.752	452.409	428.308	-2030.225	-811.103	9.629
4500	107.777	552.174	454.599	439.085	-2028.352	-783.415	9.094
4600	107.791	554.543	456.746	449.863	-2026.414	-755.777	8.582
4700	107.803	556.861	458.852	460.643	-2024.413	-728.170	8.093
4800	107.815	559.131	460.917	471.424	-2022.352	-700.612	7.624
4900	107.826	561.354	462.944	482.206	-2020.227	-673.103	7.175
5000	107.836	563.532	464.934	492.989	-2018.046	-645.627	6.745
5100	107.846	565.668	466.889	503.773	-2015.808	-618.208	6.332
5200	107.855	567.762	468.809	514.558	-2013.514	-590.815	5.935
5300	107.864	569.817	470.695	525.344	-2011.167	-563.490	5.553
5400	107.872	571.833	472.549	536.131	-2008.767	-536.186	5.186
5500	107.879	573.812	474.373	546.918	-2006.316	-508.942	4.833
5600	107.887	575.756	476.166	557.707	-2003.819	-481.739	4.493
5700	107.894	577.666	477.930	568.496	-2001.273	-454.582	4.166
5800	107.900	579.542	479.665	579.285	-1998.683	-427.459	3.850
5900	107.907	581.387	481.374	590.076	-1996.048	-400.409	3.545
6000	107.913	583.200	483.056	600.867	-1993.372	-373.381	3.251

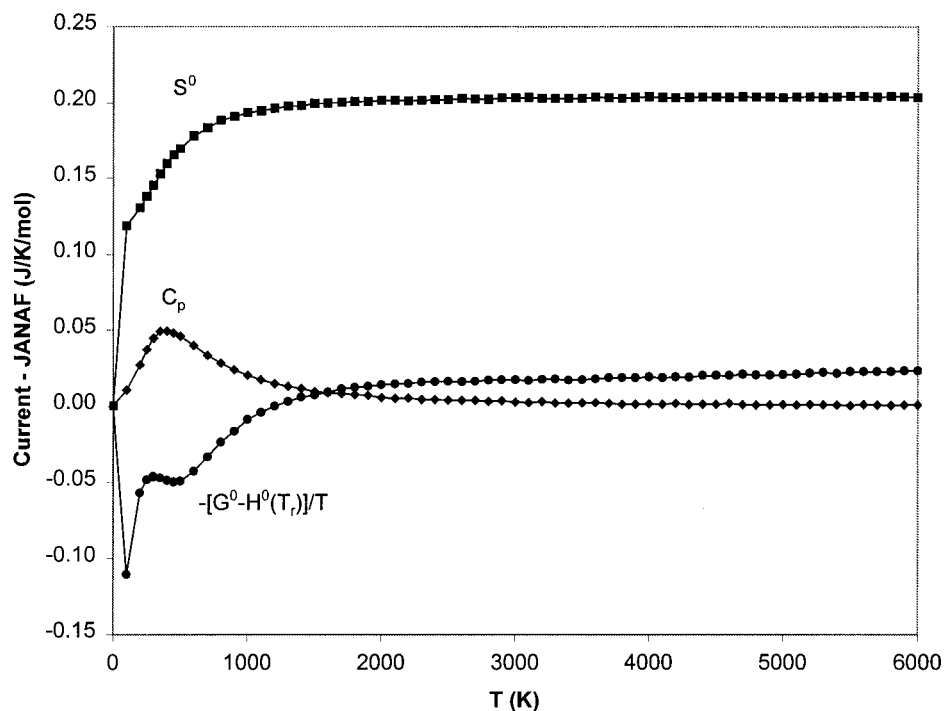


FIG. 4. Difference between our calculation and the NIST-JANAF Thermochemical Tables<sup>25</sup> for the heat capacity, entropy, and Gibbs energy function temperature dependence for  $\text{SiF}_4$ .

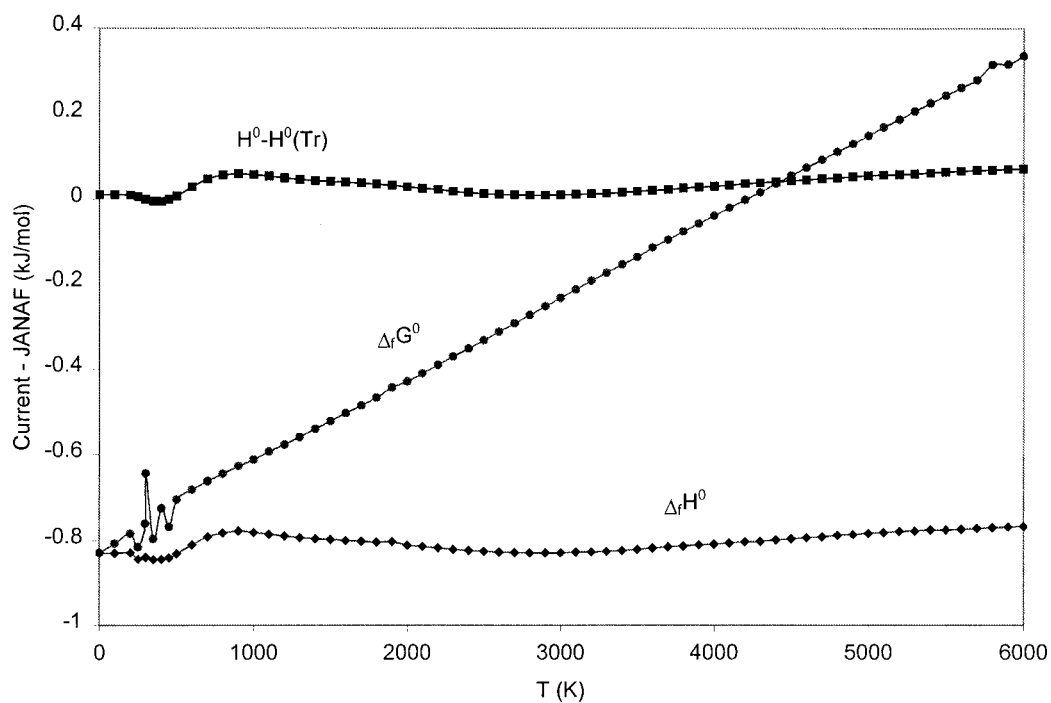


FIG. 5. Difference between our calculation and the NIST-JANAF Thermochemical Tables<sup>25</sup> for the enthalpy, enthalpy of formation, and the Gibbs energy of formation for  $\text{SiF}_4$ .

TABLE 7. SiF<sub>4</sub> (ideal gas) coefficients, CHEMKIN format

	Low (300–1000 K)	High (1000–5000 K)
$a_1$	2.182 457 35E+00	1.077 615 15E+01
$a_2$	3.378 291 81E-02	2.402 784 65E-03
$a_3$	-4.689 755 45E-05	-1.025 031 39E-06
$a_4$	3.173 358 34E-08	1.951 170 21E-10
$a_5$	-8.497 066 84E-12	-1.375 598 96E-14
$a_6$	-1.961 315 04E+05	-1.981 392 82E+05
$a_7$	1.333 659 03E+01	-2.919 303 08E+01

TABLE 8. Phase change information for SiF<sub>4</sub>

Quantity	Value	Units	References
Boiling point <sup>a</sup>	177.83	K	31, 15
Triple point	186.35	K	31, 15
$\Delta H_{\text{Sub}}$	26.087	kJ mol <sup>-1</sup>	31, 15
$\Delta S_{\text{Sub}}$	146.682	J K <sup>-1</sup> mol <sup>-1</sup>	31, 15
$\Delta H_{\text{Vap}}$	15.802	kJ mol <sup>-1</sup>	31, 15
$\Delta S_{\text{Vap}}$	91.503	J K <sup>-1</sup> mol <sup>-1</sup>	31, 15

<sup>a</sup>Temperature at which vapor pressure is 1.0 bar.

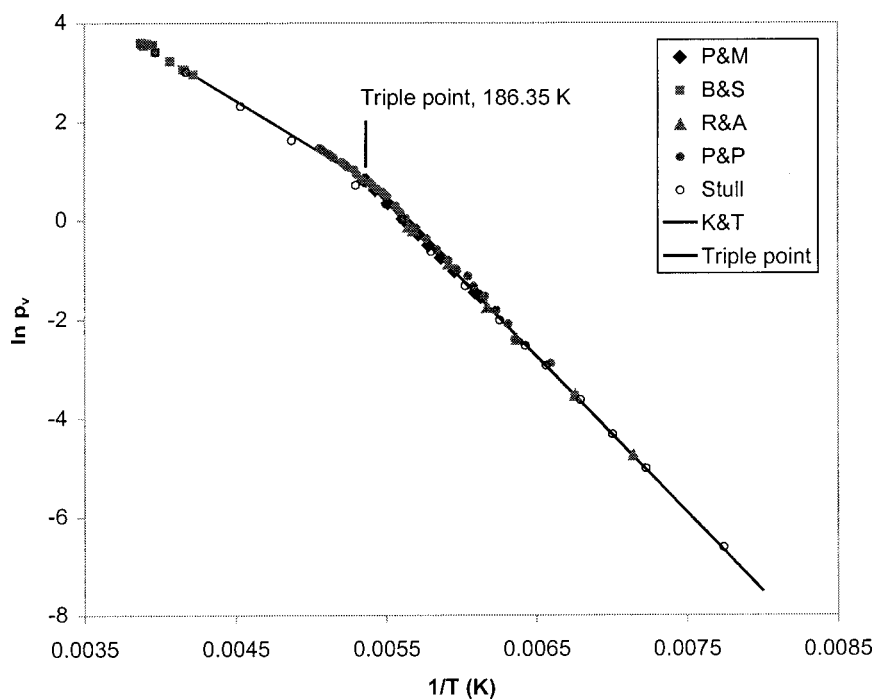


FIG. 6. Vapor pressure of SiF<sub>4</sub> over liquid and solid. Sources: P&M,<sup>15</sup> B&S,<sup>34</sup> R&A,<sup>33</sup> P&P,<sup>35</sup> Stull,<sup>29</sup> K&T.<sup>32</sup>

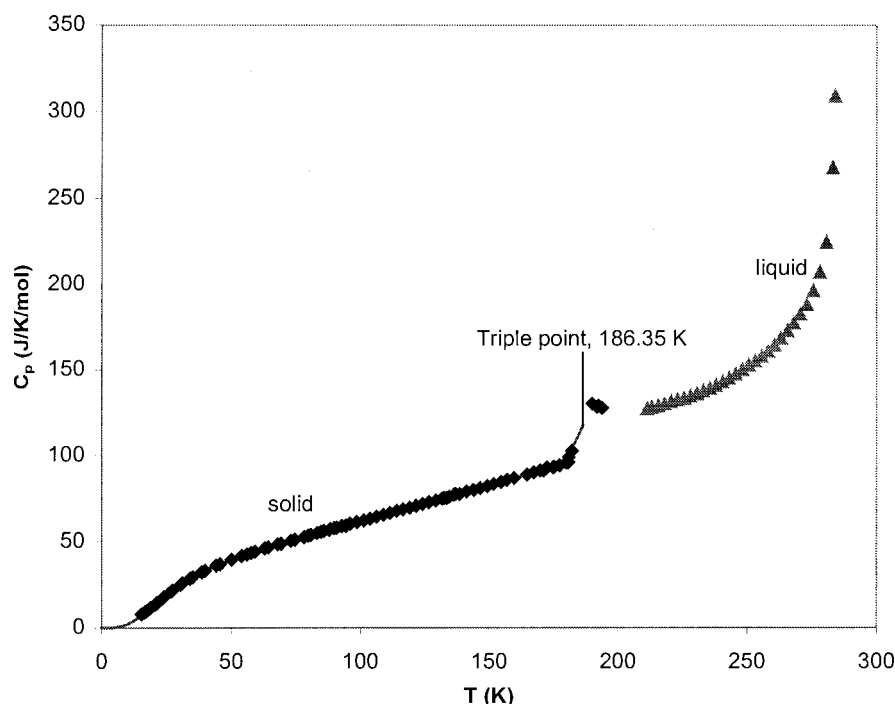


FIG. 7. Heat capacity of  $\text{SiF}_4$  in condensed phases as measured by Pace and Moser<sup>15</sup> (solid) and Yaws<sup>16</sup> (liquid).

harmonic density of states. We use standard statistical mechanical procedures<sup>38</sup> to calculate the thermochemical parameters in the NIST–JANAF Thermochemical Tables<sup>25</sup> format. The results are given in Table 12. The differences between the harmonic (Table 6) and the anharmonic (Table 12) assumptions only become significant at temperatures above 1000 K. Figure 10 shows the heat capacity for the two assumptions and Fig. 11 shows the differences for enthalpy, heat capacity, and entropy.

## 6. Discussion of Results

The main conclusion drawn from the results presented here is confirmation of the previously known values of the thermochemical parameters for  $\text{SiF}_4$  and  $\text{Si}_2\text{F}_6$ . Some minor differences, in the parameters for both species in the gas phase, were determined. With the more reliable experimental spectroscopic and calorimetric measurements used in constructing the tables of the parameters, the current values are on a much better foundation than the earlier results. Further-

more, the thermochemical parameters for the condensed phases of both species were not known before this work.

The discussion of the earlier work by others of the sublimation and vapor pressures for  $\text{SiF}_4$  gives a clearer assessment of the accuracy of the different experimental measurements. Although the measurements of Pace and Moser<sup>15</sup> were thought to be most correct, a nonjudgmental average of all measurements would result in a vapor pressure curve that was very close to the Pace and Moser measurements. The results of Stull<sup>29</sup> were too low in the region of the triple point, but this error was approximately canceled by the high values of Patnode and Papish.<sup>35</sup> The compilation of Lide and Kehiaian<sup>42</sup> takes this approach.

The authors, and others, have discounted the vapor pressure measurements of Stull<sup>29</sup> for  $\text{SiF}_4$ , but the Stull sublimation pressure measurements for  $\text{Si}_2\text{F}_6$  were used to derive the entropy and enthalpy of sublimation. This is because no better measurements exist. A confirmation of the Stull measurements would make the thermochemical properties reported here more secure.

With the enthalpies of formation in Tables 2 and 7 and

TABLE 9. Thermochemical properties of silicon tetrafluoride (solid) (enthalpy reference temperature =  $T_r = 298.15$  K, standard state pressure =  $p^0 = 0.1$  MPa)

$T/\text{K}$	$\text{J K}^{-1} \text{mol}^{-1}$		$\text{kJ mol}^{-1}$		$\log K_f$
	$C_p^0$	$S^0$	$\Delta_f H^0$	$\Delta_f G^0$	
0	0.000	0.000	-1637.598	-1637.598	infinite
50	39.599	40.479	-1632.583	-1624.838	1697.434
100	61.690	69.495	-1639.394	-1611.886	841.952
150	82.510	92.099	-1640.018	-1598.278	556.562
186.351	16.000	106.768	-1640.363	-1588.314	445.205

TABLE 10. Thermochemical properties of silicon tetrafluoride (liquid) (enthalpy reference temperature =  $T_r = 298.15$  K, standard state pressure =  $p^0 = 0.1$  MPa)

$T/\text{K}$	$\text{J K}^{-1} \text{mol}^{-1}$		$\text{kJ mol}^{-1}$		$\log K_f$
	$C_p^0$	$S^0$	$\Delta_f H^0$	$\Delta_f G^0$	
186.351	16.000	160.345	-1630.257	-1588.192	445.171
200	124.332	165.456	-1630.296	-1584.793	413.900
225	133.635	173.751	-1630.447	-1579.343	366.646
250	150.636	181.240	-1630.620	-1573.424	328.745

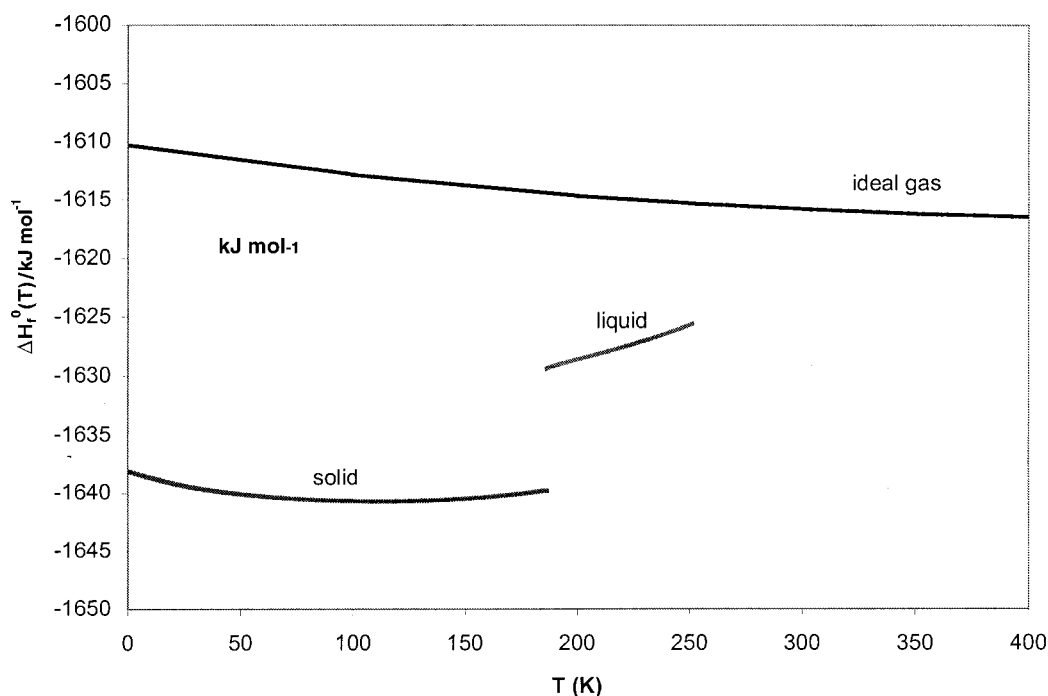


FIG. 8. Enthalpy of formation for the three phases of  $\text{SiF}_4$  in the temperature range from 0 K to 400 K.

similar information for  $\text{SiF}_2$  from the NIST–JANAF Thermochemical Tables,<sup>25</sup> the enthalpy change for reaction



can be calculated; the value is  $141.2 \text{ kJ mol}^{-1}$  at 298.15 K. This is a small value. The stability of  $\text{Si}_2\text{F}_6$  is probably enhanced by additional energy required to promote the reaction. This is confirmed by the fact that Bains *et al.*<sup>43</sup> report an activation energy for the reaction that is  $50 \text{ kJ mol}^{-1}$  greater than the enthalpy change.

The highly accurate spectroscopic measurements of Tosa *et al.*<sup>21</sup> for  $\text{Si}_2\text{F}_6$  and McDowell *et al.*<sup>13</sup> for  $\text{SiF}_4$  were used. It is unlikely that any significant improvement would follow from more accurate measurements. Even less accurate values of the vibrational frequencies still give reasonable results. The calculated frequencies of Ho and Melius<sup>17</sup> gave results

for entropy and heat capacity for  $\text{Si}_2\text{F}_6$  that were about 15 J/K/mol greater than our values (Figs. 1 and 2).

For  $\text{SiF}_4$  the vibrational frequencies available for the NIST–JANAF Thermochemical Tables<sup>25</sup> averaged only about 0.1% greater than the more accurate values used here<sup>13</sup> (Table 6). The lower frequencies increased the heat capacity, entropy, and enthalpy by at most 0.09 J/K/mol (Fig. 5). Vibrational frequencies were available earlier<sup>44</sup> from Raman measurements on liquid  $\text{SiF}_4$ . These frequencies were less than 0.4% greater than the ones we used.<sup>13</sup> Using the liquid frequencies would decrease the heat capacity, entropy, and enthalpy by less than 0.4 J/K/mol.

A comment about anharmonic correction for  $\text{SiF}_4$  (Sec. 5.3, Table 12) is appropriate.  $\text{SiF}_4$  probably has the lowest anharmonicity of any polyatomic molecule because of its very strong bonds. Some of the anharmonic cross terms are also positive. The effects we see (Figs. 10 and 11) for  $\text{SiF}_4$  are probably less than for any other polyatomic molecule. The anharmonicity effect is mainly at high temperatures. This means that it is mostly the high-energy vibrational states that are most effected. It is the highly excited states that are most important to consider in chemical reactions. Reaction rate theories for both unimolecular and bimolecular reactions that employ an activated complex may at some point need to consider the effect of anharmonicity. The evidence from  $\text{SiF}_4$ , however, is not compelling.

Another caveat about the anharmonic correction is that the method used here was only a second order correction and not an exact solution. Higher order spectroscopic terms are not available for polyatomic molecules.

TABLE 11. Anharmonicity constants for  $\text{SiF}_4$  (ideal gas)

Symbol	Value/cm <sup>-1</sup>	Uncertainty/cm <sup>-1</sup>	Reference
$x_{11}$	-0.57	0.05	13
$x_{12}$	-0.6	1.2	13
$x_{13}$	-3.8	0.3	13
$x_{14}$	+0.64	0.07	13
$x_{22}$	0.0	0.5	13
$x_{23}$	-1.5	1.0	13
$x_{24}$	0.0	0.5	13
$x_{33}$	-3.0058	0.0007	13
$x_{34}$	-0.5	0.4	13
$x_{44}$	-0.22	0.10	13



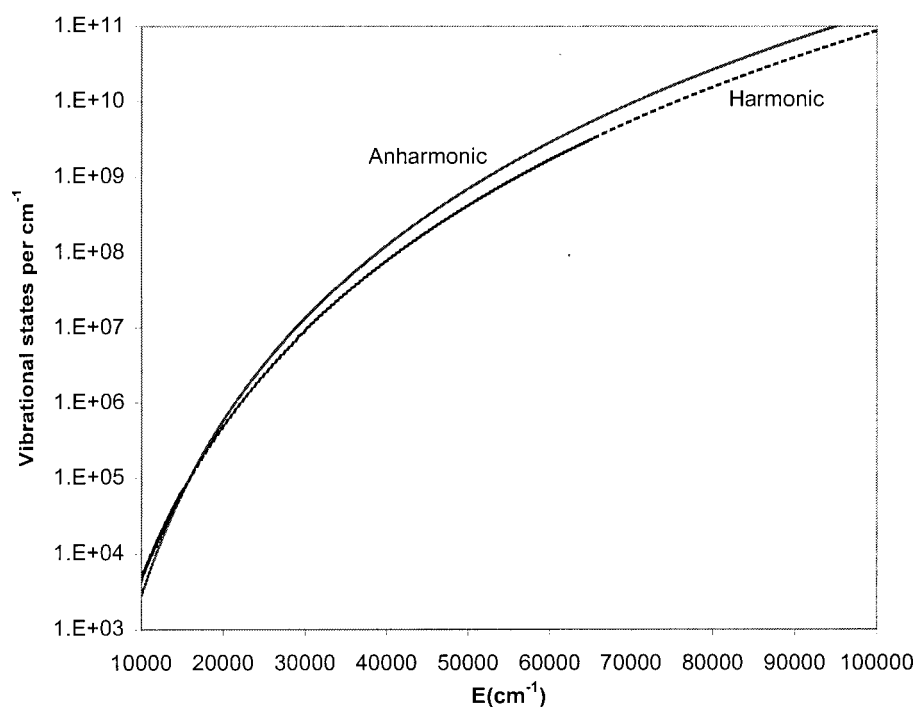


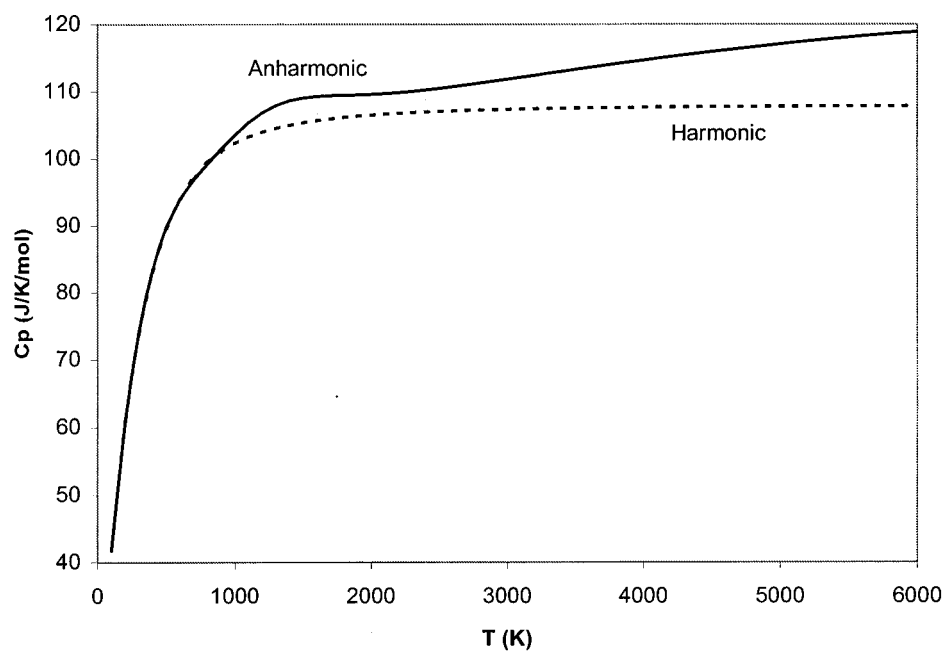
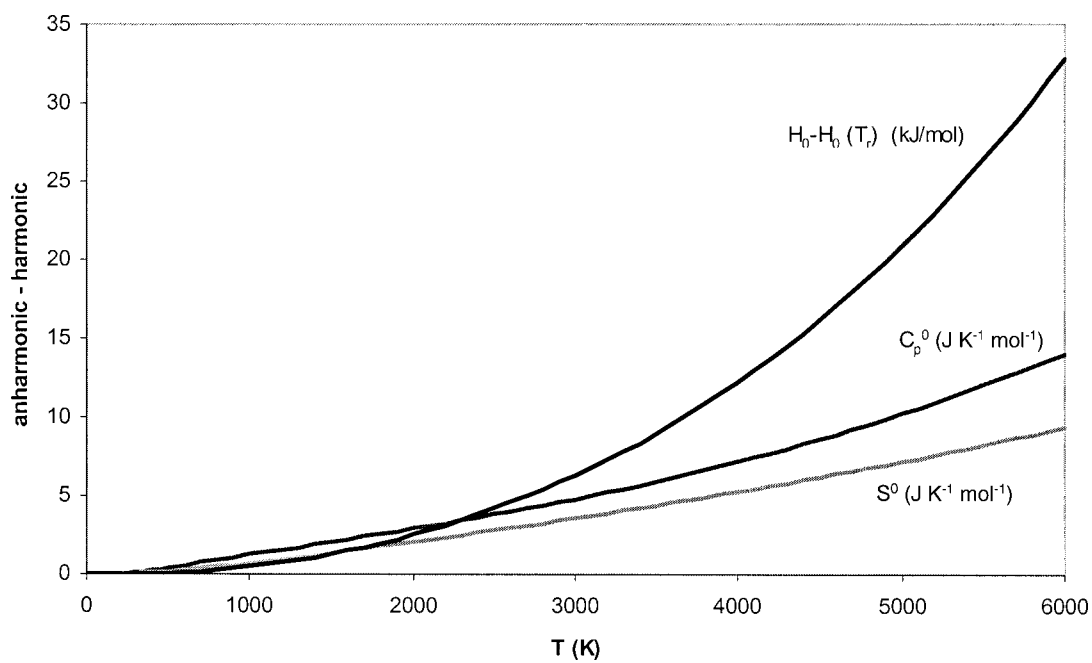
FIG. 9. Density of vibrational states of  $\text{SiF}_4$  for harmonic and anharmonic assumptions up to  $100\,000\text{ cm}^{-1}$ .

TABLE 12. Thermochemical properties of silicon tetrafluoride (ideal gas, anharmonic oscillator) (enthalpy reference temperature =  $T_r = 298.15\text{ K}$ , standard state pressure =  $p^0 = 0.1\text{ MPa}$ )

$T/\text{K}$	$\text{J K}^{-1}\text{ mol}^{-1}$			$\text{kJ mol}^{-1}$			$\log K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
0	0.000	0.000	infinite	-15.367	-1609.482	-1610.273	infinite
100	41.827	220.811	339.260	-11.845	-1612.039	-1600.455	835.981
200	60.929	256.102	289.316	-6.642	-1613.874	-1587.291	414.552
250	67.964	270.475	284.137	-3.416	-1614.503	-1580.315	330.184
298.15	73.764	282.954	282.954	0.000	-1614.982	-1573.601	275.684
300	73.969	283.411	282.956	0.137	-1614.999	-1573.339	273.939
350	79.095	295.209	283.875	3.967	-1615.407	-1566.307	233.755
400	83.423	306.062	285.980	8.033	-1615.662	-1559.073	203.591
450	87.043	316.104	288.776	12.298	-1615.870	-1551.948	180.143
500	90.062	325.436	291.981	16.728	-1615.977	-1544.677	161.369
600	94.691	342.289	298.992	25.978	-1616.048	-1530.232	133.216
700	97.971	357.146	306.260	35.621	-1615.957	-1515.781	113.108
800	100.360	370.393	313.463	45.544	-1615.762	-1501.339	98.026
900	102.151	382.322	320.463	55.673	-1615.503	-1486.918	86.298
1000	103.532	393.159	327.199	65.959	-1615.209	-1472.514	76.916
1100	104.628	403.080	333.652	76.370	-1614.900	-1458.128	69.240
1200	105.519	412.223	339.824	86.879	-1614.574	-1443.759	62.845
1300	106.262	420.700	345.724	97.469	-1614.265	-1429.405	57.434
1400	106.892	428.598	351.365	108.128	-1613.969	-1415.058	52.796
1500	107.438	435.992	356.762	118.844	-1613.698	-1400.721	48.777
1600	107.918	442.941	361.934	129.612	-1613.449	-1386.385	45.260
1700	108.349	449.497	366.893	140.427	-1663.409	-1371.603	42.144
1800	108.740	455.701	371.656	151.281	-1662.996	-1354.296	39.300

TABLE 12. Thermochemical properties of silicon tetrafluoride (ideal gas, anharmonic oscillator) (enthalpy reference temperature= $T_r=298.15$  K, standard state pressure= $p^0=0.1$  MPa)—Continued

$T/K$	$\text{J K}^{-1} \text{mol}^{-1}$			$\text{kJ mol}^{-1}$			$\log K_f$
	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_f H^0$	$\Delta_f G^0$	
1900	109.099	461.590	376.236	162.173	-1662.875	-1337.302	36.764
2000	109.434	467.195	380.645	173.100	-1662.127	-1319.704	34.467
2100	109.749	472.542	384.895	184.060	-1661.660	-1302.424	32.396
2200	110.049	477.654	388.996	195.049	-1661.169	-1285.150	30.513
2300	110.337	482.552	392.957	206.069	-1660.646	-1267.883	28.794
2400	110.616	487.254	396.789	217.116	-1660.083	-1250.625	27.219
2500	110.886	491.775	400.499	228.191	-1659.477	-1233.380	25.770
2600	111.151	496.129	404.094	239.293	-1658.819	-1216.142	24.432
2700	111.412	500.329	407.581	250.422	-1658.105	-1198.915	23.194
2800	111.670	504.385	410.966	261.576	-1657.327	-1181.701	22.044
2900	111.925	508.308	414.255	272.756	-1656.477	-1164.503	20.975
3000	112.180	512.108	417.455	283.961	-1655.551	-1147.317	19.976
3100	112.435	515.791	420.567	295.191	-1654.540	-1130.146	19.042
3200	112.690	519.364	423.599	306.448	-1653.437	-1112.993	18.167
3300	112.946	522.836	426.554	317.729	-1652.236	-1095.855	17.346
3400	113.204	526.211	429.435	329.037	-1650.927	-1078.750	16.573
3500	113.466	529.497	432.247	340.370	-1649.507	-1061.657	15.844
3600	113.730	532.697	434.993	351.730	-1647.978	-1044.585	15.161
3700	113.999	535.816	437.677	363.116	-1647.343	-1027.533	14.520
3800	114.272	538.860	440.300	374.530	-1646.603	-1010.500	13.916
3900	114.551	541.832	442.865	385.971	-1645.758	-993.484	13.345
4000	114.836	544.736	445.376	397.441	-1644.808	-976.483	12.803
4100	115.127	547.575	447.834	408.939	-1643.753	-959.495	12.287
4200	115.424	550.353	450.242	420.466	-1642.593	-942.528	11.794
4300	115.727	553.072	452.601	432.023	-1641.328	-925.580	11.323
4400	116.039	555.736	454.915	443.612	-1640.058	-908.650	10.871
4500	116.358	558.348	457.185	455.231	-1638.683	-891.736	10.437
4600	116.683	560.909	459.412	466.883	-1637.203	-874.837	10.020
4700	117.016	563.421	461.598	478.568	-1635.618	-857.952	9.618
4800	117.356	565.889	463.745	490.287	-1634.028	-841.080	9.230
4900	117.703	568.312	465.855	502.040	-1632.433	-824.220	8.855
5000	118.055	570.693	467.928	513.828	-1630.833	-807.371	8.493
5100	118.414	573.035	469.966	525.651	-1629.228	-790.532	8.143
5200	118.779	575.338	471.970	537.511	-1627.618	-773.702	7.804
5300	119.148	577.604	473.942	549.407	-1626.003	-756.880	7.475
5400	119.522	579.834	475.882	561.340	-1624.383	-740.066	7.155
5500	119.900	582.031	477.792	573.312	-1622.758	-723.260	6.843
5600	120.281	584.195	479.673	585.321	-1621.128	-706.461	6.539
5700	120.665	586.327	481.525	597.368	-1619.493	-689.669	6.241
5800	121.052	588.429	483.350	609.454	-1617.853	-672.892	5.949
5900	121.440	590.502	485.149	621.578	-1616.208	-656.130	5.662
6000	121.829	592.546	486.922	633.742	-1614.558	-639.382	5.380

FIG. 10. Heat capacity for anharmonic and harmonic assumptions for  $\text{SiF}_4$ .FIG. 11. Difference between anharmonic and harmonic assumptions for enthalpy, entropy, and heat capacity for  $\text{SiF}_4$ .

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