

Thermochemical Data on Gas Phase Compounds of Sulfur, Fluorine, Oxygen, and Hydrogen Related to Pyrolysis and Oxidation of Sulfur Hexafluoride

John T. Herron

Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899

Received March 21, 1986; revised manuscript received August 20, 1986

Thermochemical data on selected gas phase compounds containing sulfur, fluorine, oxygen, and hydrogen are evaluated. These are of particular relevance to plasma chemistry and SF₆ dielectric breakdown. Values of the enthalpies of formation and the entropy are provided at 298 K. Where no experimental data are available, methods for estimation have been developed for deriving the enthalpy of formation. Data are tabulated for 36 substances.

Key words: data; evaluation; fluorine; hydrogen; oxygen; sulfur; sulfur hexafluoride; thermochemistry.

Contents

1. Introduction	1	2. Bond strengths in SF _x , OSF _x , O ₂ SF _x , and S ₂ F _x compounds	3
2. The Series SF _x (x = 0 to 6)	2		
3. The Series OSF _x (x = 0 to 5)	4		
4. The Series S ₂ F _x (x = 0 to 10)	4		
5. Miscellaneous S-F-O Compounds	6		
6. Summary and Conclusions	6		
7. Acknowledgments	6		
8. References	6		

List of Tables

1. $\Delta_f H_{298}^\circ$ and S_{298}° for some S-F-O-H molecules, radicals, and related compounds	2
---	---

List of Figures

1. Bond strengths in SF _x , OSF _x , and O ₂ SF _x compounds as a function of <i>n</i> , where <i>n</i> is the sum of the number of S-F bonds and twice the number of S = O bonds	3
2. $\Delta_f H_{298}^\circ$ for the series S ₂ F _x , x = 0 to 10	5

1. Introduction

Detailed modeling of the physical and chemical processes occurring in plasmas, chemical vapor deposition, and dielectric breakdown of sulfur hexafluoride requires an evaluated thermochemical and kinetic data base. This review provides a thermochemical data base applicable to the problem of dielectric breakdown in sulfur hexafluoride, an important gaseous insulator used in large switches and other high-voltage devices.

The starting point for this review is the earlier review of Benson¹ and the JANAF Thermochemical Tables.²⁻⁵ The review of Mills,⁶ which contains data on sulfur fluorine compounds, is more limited in coverage, and was not used. Since there are few experimental data available for the compounds

of interest, particularly as regards enthalpies of formation, it has been necessary to develop and apply methods for estimating these properties.

Data are presented in tabular form, listing the standard enthalpies of formation $\Delta_f H^\circ$ and entropy S° , all referred to 298.15 K and 1 atm. (Throughout the text, in using $\Delta_f H^\circ$ and S° without a subscript specifying temperature, or with the subscript 298, it is understood to refer to 298.15 K.) Data are reported in SI units, using the conversion factors 1 cal \equiv 4.184 J and 1 eV \equiv 96.485 J/mol. The source of the data is given, and is discussed in detail in the text as appropriate. Except for the series SF_x (x = 0 to 6), and some of the S₂F_x (x = 0 to 10) compounds, there are relatively few values based on experiment. Many of the enthalpies given in the tables are estimates. All such data are enclosed in parentheses.

In addition to tables of enthalpies and entropies, tables of bond strengths are provided based on experimental observation or derived from the tables of enthalpies of formation.

©1987 by the U. S. Secretary of Commerce on behalf of the United States. This copyright is assigned to the American Institute of Physics and the American Chemical Society.
Reprints available from ACS; see Reprints List at back of issue.

For the bond scission reaction $AB \rightarrow A + B$, where A and B may be atoms or free radicals, the bond strength is defined as

$$D_{298}^{\circ}(A-B) = \Delta H_{298}^{\circ} \\ = \Delta_f H_{298}^{\circ}(A) + \Delta_f H_{298}^{\circ}(B) - \Delta_f H_{298}^{\circ}(AB),$$

where ΔH_{298}° is the enthalpy of reaction.

The review is divided into four sections: (1) the series SF_x ($x = 0$ to 6), (2) the series OSF_x ($x = 0$ to 5), (3) the series S_2F_x ($x = 0$ to 10), and (4) miscellaneous S, F, O compounds.

2. The Series SF_x ($x = 0$ to 6)

The starting point for considering this series is the data on F, S, SF, SF_2 , SF_4 , and SF_6 given in the JANAF Thermochemical Tables and reported here in Table 1. They are accepted without change. The important new data available for this series are the bond strengths for SF_4 and SF_6 reported by Kiang and Zare⁷ derived from studies of the chemiluminescence resulting from the reactions of SF_4 and SF_6 with metastable excited Ca and Sr atoms. From the chemilu-

minescence, the highest populated internal state of the product MF species ($M = Ca$ or Sr) was identified. By means of separate time-of-flight measurements, the translational energy of the M species, which were produced in a nozzle beam apparatus, were measured. The assumption was then made that in some collisions all the reaction exothermicity appeared in the form of chemiluminescence. Under those conditions, the internal energy in the other product (SF_{x-1}) and its translational energy were taken to be zero. This gives an upper limit to the reaction enthalpy, and if the assumption regarding internal and translation energy of the SF_{x-1} product is correct, it provides a true measure of the reaction enthalpy. Extrapolation of the data to 0 K, then yields $\Delta H_0^{\circ} = D_0^{\circ}$. They report $D_0^{\circ}(SF_3-F) = 351.9 \pm 12.6$ and $D_0^{\circ}(SF_5-F) = 381.2 \pm 13.4$ kJ mol⁻¹. From these data one calculates the enthalpies of formation of SF_3 and SF_5 at 298.15 K (using auxiliary data from the JANAF Tables²).

There are two major sources of systematic error in the measurement of bond strengths and hence enthalpies of formation using this technique. The first relates to the identifi-

TABLE 1. $\Delta_f H_{298}^{\circ}$ and S_{298}° for some S-F-O-H molecules radicals, and related compounds^a

Species	$\Delta_f H_{298}^{\circ}$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)	Source
F	78.91 ± 1.67	158.645	Ref. 5
S	276.98 ± 0.21	167.720 ± 0.034	Ref. 2
SF	13.0 ± 6.3	225.1 ± 0.8	Ref. 3
SF ₂	-296.6 ± 16.7 [-262.8 ± 23.0]	257.61 ± 0.08	Ref. 3
SF ₃	-488.3 ± 25	286.2 ± 4.2	$\Delta_f H$, Ref. 7 ^b ; S, Ref. 2
SF ₄	-763.2 ± 21	299.6 ± 0.4	Ref. 3
SF ₅	-912.5 ± 13.4	304.6 ± 8.4	$\Delta_f H$, Ref. 7 ^b ; S, Ref. 2
SF ₆	-1220.5 ± 0.8	291.6 ± 0.4	Ref. 3
S ₂	128.49 ± 0.29	228.053 ± 0.050	Ref. 2
SSF	(-10 ± 20)		
SSF ₂	-297 ± 10	292.71 ± 4.18	$\Delta_f H$, Ref. 3 ^b ; S, Ref. 3
FSSF	-286 ± 10	293.97 ± 0.08	$\Delta_f H$, Ref. 3 ^b ; S, Ref. 3
SFSF ₃	-660 ± 24 [-593 ± 33]	334 ± 4	$\Delta_f H$, Ref. 17 ^b ; S, Ref. 17
S ₂ F ₆	(-1130 ± 50)		
S ₂ F ₈	(-1570 ± 50)		
S ₂ F ₉	(-1704 ± 25)		
S ₂ F ₁₀	-2012 ± 21	397.1 ± 8.4	$\Delta_f H$, Ref. 19; S, Ref. 2
O	249.174 ± 0.100	160.950 ± 0.021	Ref. 2
FO	109 ± 42	216.61 ± 1.26	Ref. 5
FO ₂	12.6 ± 21	259.0	Ref. 5
F ₂ O	24.52 ± 1.59	247.36 ± 0.4	Ref. 5
OS	5.0 ± 1.3	221.836 ± 0.042	Ref. 2
OSF	(-207 ± 33)	(258)	Ref. 5
OSF ₂	(-494 ± 32)	279.03 ± 0.42	S, Ref. 4
OSF ₃	(-633 ± 21)	(300)	
OSF ₄	(-954 ± 16)	312.654	S, Ref. 24
OSF ₅	(-996 ± 15)	(292)	
O ₂ SF	(-428 ± 15)		
O ₂ SF ₂	-758.6 ± 8.4	283.51 ± 0.42	Ref. 4
O ₂ SF ₃	-969 ± 15		
H	217.999 ± 0.004	114.603 ± 0.017	Ref. 2
HF	-272.55 ± 0.8	173.669	Ref. 5
SF ₃ (OH)	(-1213 ± 13)		
SF ₃ (OF)	(-1089 ± 15)		
(SF ₃ O) ₂	(-2148 ± 25)		
SF ₃ O ₃ SF ₃	(-2069 ± 21)		

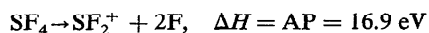
^a All values in parentheses are estimated. Values in brackets are based on appearance potential measurements (see text).

^b Recalculated from data given in referenced source.

cation of the highest excited vibrational level of the product fluoride which contributes about $\pm 4 \text{ kJ mol}^{-1}$. The other arises from the uncertainty in $D^\circ(\text{Ca-F})$ or $D^\circ(\text{Sr-F})$, which is about $\pm 8 \text{ kJ mol}^{-1}$. Improvements in the quality of these bond dissociation energies will lead to a direct improvement in the quality of the SF_x data. In this review, the values for $\Delta_f H^\circ(\text{SF}_3)$ and $\Delta_f H^\circ(\text{SF}_5)$ derived from the measurements of Kiang and Zare have been accepted. They are supported by shock-tube measurements. The JANAF value, $\Delta_f H^\circ(\text{SF}_5) = -908.3 \pm 15.1 \text{ kJ mol}^{-1}$, is based on Lyman's⁸ reinterpretation of the shock-tube study of Bott and Jacobs⁹ on the decomposition of SF_6 . It can be compared with the value which can be derived from the study of Kiang and Zare⁷ of $-912.5 \pm 13.4 \text{ kJ mol}^{-1}$. In the case of SF_3 , the older shock-tube data on SF_4 decomposition¹⁰ have not been reanalyzed in the same manner as the SF_6 data. The data are consistent with a value of $D_{298}^\circ(\text{SF}_3\text{-F}) = 326.4 \pm 12.6 \text{ kJ mol}^{-1}$, from which $\Delta_f H^\circ(\text{SF}_3) = -516.7 \pm 24.6 \text{ kJ mol}^{-1}$ can be calculated. This should be taken as a lower limit.

Bond strengths, D_{298}° , for the SF_x series are given in Table 2 and compared in Fig. 1 with S-F bond strengths in other molecules.

The major uncertainty in the data for the SF_x series is in $\Delta_f H^\circ$ for SF_4 which is uncertain by at least 21 kJ mol^{-1} . This also leads to the large uncertainty in $\Delta_f H^\circ$ for SF_3 which is derived from the reaction $\text{SF}_4 \rightarrow \text{SF}_3 + \text{F}$. There is also a problem with the enthalpy of formation of SF_2 . The value adopted here, $-296.6 \pm 16.7 \text{ kJ mol}^{-1}$, is based on an analysis³ of equilibrium data for the reaction $\text{S} + \text{SF}_2 \rightleftharpoons 2\text{SF}$.⁸ Lösling *et al.*¹² report a value for $\Delta_f H^\circ(\text{SF}_2)$ of -267 kJ mol^{-1} based on photoionization appearance potential measurements on SF_4 and SSF_2 . They reported the appearance potential of SF_2^+ from SF_4 to be 16.9 eV . If the process corresponds to:



[in this and subsequent discussions of ionization potential (IP) and appearance potential (AP) data, electrons will not be explicitly included in the equations] and as the ionization potential of SF_2 is known,¹³ i.e.,

TABLE 2. Bond strengths in SF_x , OSF_x , O_2SF_x , and S_2F_x compounds.

Bond	D_{298}° (kJ mol ⁻¹)	Bond	D_{298}° (kJ mol ⁻¹)
S-F	343 ± 7	S = S	425.5
SF-F	389 ± 18[355 ± 24] ^a	S = SF ₂	277 ± 19[311 ± 25]
SF ₂ -F	271 ± 28[304 ± 32]	FS-SF	312 ± 12
SF ₃ -F	354 ± 13	FS-SF ₃	185 ± 34[112 ± 42]
SF ₄ -F	228 ± 25	F ₂ S-SF ₃	153 ± 59
SF ₅ -F	387 ± 13	F ₃ S-SF ₅	171 ± 61
OS-F	291 ± 33	F ₅ S-SF ₅	192 ± 22
OSF-F	366 ± 17		
OSF ₂ -F	219 ± 28		
OSF ₃ -F	400 ± 13		
OSF ₄ -F	120.5 ± 5.4		
O ₂ S-F	210 ± 14		
O ₂ SF-F	410 ± 12		

^a Values in brackets are based on appearance potential measurements (see text).

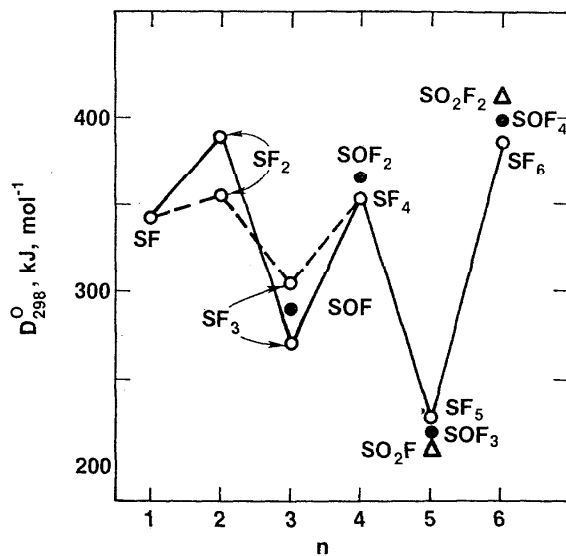
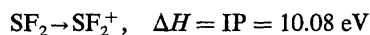
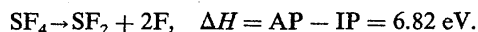


FIG. 1. Bond strengths in SF_x , OSF_x , and O_2SF_x compounds as a function of n , where n is the sum of the number of S-F bonds and twice the number of S=O bonds.



then



Using $\Delta_f H^\circ$ data from Table 1, and assigning an uncertainty of 0.1 eV to the appearance potential measurement (which should be taken as an upper limit in any case), leads to $\Delta_f H^\circ(\text{SF}_2) = -262.8 \pm 23.0 \text{ kJ mol}^{-1}$. This differs slightly from the value derived by Lösling *et al.* due to the use of different auxiliary thermochemical data. Although equilibrium measurements in general are preferable to appearance potential measurements in deriving thermochemical data, there are reasons to consider the appearance potential value. As will be pointed out in Sec. 4, Lösling *et al.*¹² have made extensive appearance potential measurements on SSF_2 , FSSF , SF_4 and SFSF_3 . Their results are in good agreement with independent equilibrium-type measurements for other systems. Also, as will be discussed in Sec. 3, S-F bond strengths derived for the OSF_x series are out of line with those that are obtained for SF_3 and SF_2 on the basis of the more negative value for $\Delta_f H^\circ(\text{SF}_2)$ (see Table 2 and Fig. 1). Since there is no basis for rejecting either set of measurements, the JANAF value for $\Delta_f H^\circ(\text{SF}_2)$ has been retained. However, I also include in the tables the values for $\Delta_f H^\circ(\text{SF}_2)$ based on the appearance potential measurements. In a similar manner dual values are given for all thermochemical quantities derived from cycles or reactions in which SF_2 was involved. These values, based on appearance potentials, are enclosed in brackets.

The entropy data given in Table 1 vary in quality. Data on SF_4 and SF_6 are probably very good based on extensive spectroscopic characterization. In the case of SF_5 , there are some vibrational data, but most of the vibrational frequencies are assigned by analogy with other known systems. This is also the case for SF_3 , SF_2 , and SF . The quoted uncertain-

ties therefore reflect the uncertainties in vibrational assignments.

3. The Series OSF_x ($x=0$ to 5)

There are no experimental data on the enthalpies of formation of any OSF_x species. There are data on several related species, however, which provide a basis for estimating the properties of the OSF_x series.

Benson¹ argued that substitution of an F atom by OH on a sulfur atom led to a decrease in stability of about 8 kJ mol^{-1} . The argument was based on comparison of $\Delta_f H^\circ(\text{O}_2\text{SF}_2) = -757 \pm 8$ and $\Delta_f H^\circ(\text{O}_2\text{S}(\text{OH})_2) = -744 \pm 8 \text{ kJ mol}^{-1}$. (These numbers are from Ref. 1). The data on O_2SF_2 and $\text{O}_2\text{S}(\text{OH})_2$ are probably reliable and support the idea of an $8 \pm 13 \text{ kJ mol}^{-1}$ difference. On that basis, one calculates (now using data from Table 1), that $\Delta_f H^\circ(\text{SF}_5\text{OH}) = -1213 \pm 13 \text{ kJ mol}^{-1}$. If $D^\circ(\text{SF}_5\text{O}-\text{H})$ is taken as the same as that in an aliphatic alcohol (435 kJ mol^{-1}), then for the reaction



and $\Delta_f H^\circ(\text{SF}_5\text{O}) = -996 \pm 15 \text{ kJ mol}^{-1}$ (this differs slightly from the value calculated in Ref. 1, reflecting different values of the auxiliary data used in the calculation).

The activation energy for the reaction $\text{SF}_5\text{O} \rightarrow \text{OSF}_4 + \text{F}$ has been reported to be $120.5 \pm 5.4 \text{ kJ mol}^{-1}$.¹⁴ Assuming that the reverse reaction has zero activation energy, and taking $\Delta_f H^\circ(\text{SF}_5\text{O}) = -996 \pm 15 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{OSF}_4) = -954 \pm 16 \text{ kJ mol}^{-1}$.

In order to estimate enthalpies for other members of the OSF_x series, it is necessary to know the S-F bond strengths in these compounds. There are two sets of direct measurements. The bond dissociation energy $D_0^\circ(\text{OSF}-\text{F}) = 361.9 \pm 16.7 \text{ kJ mol}^{-1}$, was reported by Kiang and Zare.⁷ No details were given as to the measurement, although the technique was the same as that discussed in Sec. 2 on bond dissociation energies in SF_4 and SF_6 . At 298 K, $D^\circ(\text{OSF}-\text{F}) = 366.1 \pm 16.7 \text{ kJ mol}^{-1}$. Benson,¹ in a reanalysis of the shock-tube data of Wray and Feldman¹⁵ on the pyrolysis of SO_2F_2 , estimated that $D_{298}^\circ(\text{O}_2\text{SF}-\text{F})$ was close to 418 kJ mol^{-1} . Allowing that it could be somewhat lower, I have chosen $D_{298}^\circ(\text{O}_2\text{SF}-\text{F}) = 410 \text{ kJ mol}^{-1}$ with an estimated uncertainty of 12 kJ mol^{-1} .

Comparing $D^\circ(\text{O}_2\text{SF}-\text{F})$ with $D^\circ(\text{SF}_5-\text{F})$ and $D^\circ(\text{OSF}-\text{F})$ with $D^\circ(\text{SF}_3-\text{F})$ (see Table 2), it can be seen that substitution of an oxygen atom for a pair of fluorine atoms leads to about an 11 kJ mol^{-1} strengthening of the S-F bond. This can be used to estimate $D^\circ(\text{OSF}_3-\text{F}) = D^\circ(\text{SF}_5-\text{F}) + 11 = 400 \pm 13 \text{ kJ mol}^{-1}$. Then from the

reaction $\text{OSF}_4 \rightarrow \text{OSF}_3 + \text{F}$, the enthalpy of formation of OSF_3 may be calculated.

To proceed further, it is necessary to know $D^\circ(\text{OSF}_2-\text{F})$. It is expected that this bond, by analogy with the bonds in the SF_x series, would be considerably weaker than $D^\circ(\text{OSF}_3-\text{F})$. Some idea as to the difference in the first and second S-F bond strengths can be had from a consideration of the bond strengths in O_2SF_2 . The sum of S-F bond strengths is the heat of reaction for $\text{O}_2\text{SF}_2 \rightarrow \text{O}_2\text{S} + 2\text{F}$, i.e., $620 \pm 8 \text{ kJ mol}^{-1}$. If the estimate for the first bond energy given above of $410 \pm 12 \text{ kJ mol}^{-1}$ is valid, then the second bond strength is $210 \pm 14 \text{ kJ mol}^{-1}$. I have chosen $D^\circ(\text{OSF}_2-\text{F})$ to lie between $D^\circ(\text{SF}_4-\text{F})$ and $D^\circ(\text{O}_2\text{S}-\text{F})$ at $219 \pm 28 \text{ kJ mol}^{-1}$. It follows that $\Delta_f H^\circ(\text{OSF}_2) = -494 \pm 32 \text{ kJ mol}^{-1}$. Using the measured value for $D^\circ(\text{OSF}-\text{F})$ it follows that $\Delta_f H^\circ(\text{OSF}) = -207 \pm 33$.

JANAF⁴ gives $\Delta_f H^\circ(\text{OSF}_2) = -544 \pm 105 \text{ kJ mol}^{-1}$ based on calculated increments in $\Delta_f H^\circ$ between OSF_2 and O_2SF_2 . The present value is probably better, but the uncertainties in either case are unfortunately large.

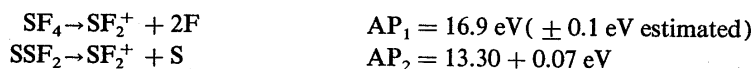
Entropy data for compounds in the series OSF_x are limited. Good values exist for OSF_2 and OSF_4 (as well as O_2SF_2) based on frequencies assigned on the basis of experiment. Comparison of the values for the SF_x and OSF_{x-1} series suggests a rough correlation which could provide a basis for estimating values based on the observation that substitution of an oxygen atom for a fluorine atom does not change in the entropy more than about $8 \text{ kJ mol}^{-1} \text{ K}^{-1}$. On this basis one can roughly estimate that $S^\circ(\text{OSF}) \approx 258$, $S^\circ(\text{OSF}_3) \approx 300$, and $S^\circ(\text{OSF}_5) \approx 292 \text{ J mol}^{-1} \text{ K}^{-1}$.

4. The Series S_2F_x ($x=0$ to 10)

The S_2F_x series is not well characterized in terms of basic thermochemical data although there are spectroscopic and equilibrium data available for several members.

Enthalpies of formation of FSSF and SSF_2 have been reported by Lösling *et al.*¹² on the basis of appearance potential measurements (using photoionization) and a direct measurement of the equilibrium $\text{SSF}_2 \rightleftharpoons \text{FSSF}$. For the latter, they report $\Delta H_{298}^\circ = 11.3 + 1.5 \text{ kJ mol}^{-1}$. The appearance potential measurements yielded $\Delta_f H^\circ(\text{SSF}_2) = -297$, and $\Delta_f H^\circ(\text{FSSF}) = -291 \text{ kJ mol}^{-1}$. Since the equilibrium measurement is the "best" data, the procedure chosen here is to calculate $\Delta_f H^\circ(\text{SSF}_2)$ from the appearance potential data, and then calculate $\Delta_f H^\circ(\text{FSSF})$ using the equilibrium data. There are two sets of relevant measurements from which $\Delta_f H^\circ(\text{SSF}_2)$ may be obtained.

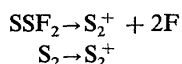
Set 1. Based on the appearance potentials of SF_2^+ from SSF_2 and SF_4 :



$$\begin{array}{l} \text{Difference:} \\ \text{SF}_4 - \text{SSF}_2 \rightarrow 2\text{F} - \text{S} \end{array} \quad \Delta H = \text{AP}_1 - \text{AP}_2 = 347.3 \pm 11.8 \text{ kJ mol}^{-1}$$

$$\begin{array}{l} \Delta_f H^\circ(\text{SSF}_2) = \Delta H - 2\Delta_f H^\circ(\text{F}) + \Delta_f H^\circ(\text{SF}_4) \\ = 299 \pm 25 \text{ kJ mol}^{-1}. \end{array}$$

Set 2. Based on the appearance potential of S_2^+ from SSF_2 and the ionization potential¹⁶ of S_2 :



$$\begin{array}{l} AP_3 = 15.42 \pm 0.05 \text{ eV} \\ IP = 9.36 \pm 0.02 \text{ eV} \end{array}$$

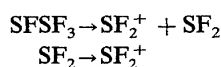
Difference:

$$\begin{array}{l} SSF_2 - S_2 - 2F \\ \Delta_f H^\circ(SSF_2) = -\Delta H + 2\Delta_f H^\circ(F) + \Delta_f H^\circ(S_2) \\ = -297 \pm 5 \text{ kJ mol}^{-1} \end{array}$$

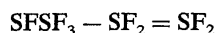
$$\Delta H = AP_3 - IP = 585 \pm 5 \text{ kJ mol}^{-1}$$

The assignment of uncertainties in the two calculations is somewhat arbitrary since the reported uncertainties in measured appearance potentials are no guarantee that the true onset was accurately obtained. The second measurement, since it did not involve using the already uncertain value ($\pm 21 \text{ kJ mol}^{-1}$) of $\Delta_f H^\circ(SF_4)$ is probably the better. $\Delta_f H^\circ(SSF_2)$ is taken as $-297 \pm 10 \text{ kJ mol}^{-1}$. It follows that $\Delta_f H^\circ(FSSF) = -286 \pm 10 \text{ kJ mol}^{-1}$.

For the reaction $SFSF_3 \rightleftharpoons 2SF_2$ Gombler *et al.*¹⁷ report



Difference:



that $K_p(298) = 2.5 \times 10^{-3} \text{ atm}$. They also report that $S_{298}^\circ(SFSF_3) = 334 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. Using $S_{298}^\circ(SF_2) = 257.61 \pm 0.08 \text{ J mol}^{-1} \text{ K}^{-1}$ from Table 1 and the equilibrium constant, one obtains, through the relationships $\Delta G = -RT \ln K_p$, and $\Delta H = \Delta G + T\Delta S$, $\Delta H_{298}^\circ = 66.9 \pm 4.2 \text{ kJ mol}^{-1}$. This value is supported by appearance potential data of Lösling *et al.*¹² They reported the appearance potential of SF_2^+ from $SFSF_3$ to be $10.80 \pm 0.05 \text{ eV}$. The heat of reaction can be obtained from the cycle:

$$\begin{array}{l} AP_4 = 10.80 \pm 0.05 \text{ eV} \\ IP_2 = 10.08 \text{ eV (Ref. 13)} \end{array}$$

$$\Delta H = AP_4 - IP_2 = 69.5 \text{ kJ mol}^{-1}$$

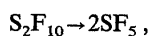
Accepting the equilibrium-based value of $66.9 \pm 4.2 \text{ kJ mol}^{-1}$ for the heat of reaction, I calculate $\Delta_f H^\circ(SFSF_3) = -660 \pm 24 \text{ kJ mol}^{-1}$ using $\Delta_f H^\circ(SF_2) = -296.6 \pm 16.7 \text{ kJ mol}^{-1}$, and $\Delta_f H^\circ(SFSF_3) = -593 \pm 32 \text{ kJ mol}^{-1}$ using $\Delta_f H^\circ(SF_2) = -262.8 \pm 23.0 \text{ kJ mol}^{-1}$. The latter value is enclosed in brackets in Table 1.

The enthalpy of formation of S_2F_{10} was derived by Benson and Bott¹⁸ from the equilibrium constant estimated for the reaction



Following Benson, the JANAF Tables² gives $\Delta_f H^\circ(S_2F_{10}) = -2064.4 \pm 29.3 \text{ kJ mol}^{-1}$.

However, from a reanalysis of the data on the pyrolysis of S_2F_{10} , the enthalpy for the reaction,



has been estimated to be $187.0 \pm 9.6 \text{ kJ mol}^{-1}$ at 444 K.¹⁹ This is close to the measured activation energy for the overall reaction of $188\text{--}209 \text{ kJ mol}^{-1}$. Accepting that $\Delta_f H^\circ(SF_5)$ is that given in Table 1, one can arrive at a different value for $\Delta_f H^\circ(S_2F_{10})$, viz., $-2012 \pm 21 \text{ kJ mol}^{-1}$. I am inclined to put greater credence on the data derived from the kinetic analysis and suggest $\Delta_f H^\circ(S_2F_{10}) = -2012 \pm 21 \text{ kJ mol}^{-1}$.

For the remainder of the series, enthalpies of formation must be estimated on the basis of bond energies and the properties of homologous series.

If the bond strength $D^\circ(SSF-F)$ is taken to be equal to $D^\circ(OSF-F) = 366 \pm 17 \text{ kJ mol}^{-1}$, then $\Delta_f H^\circ(SSF) = -10 \pm 20 \text{ kJ mol}^{-1}$. Similarly, if the bond strength $D^\circ(S_2F_9-F)$ is taken to be equal to $D^\circ(SF_5-F) = 387 \pm 13 \text{ kJ mol}^{-1}$, then $\Delta_f H^\circ(S_2F_9) = -1704 \pm 25 \text{ kJ mol}^{-1}$.

Data on $\Delta_f H^\circ$ for the series S_2F_x are plotted in Fig. 2 as a function of x . In the absence of any other quantitative data,

a straight line has been drawn through the points and values of $\Delta_f H^\circ$ for the intermediate compounds S_2F_6 and S_2F_8 have been interpolated. There is a report in the literature on the compound SF_3SF_3 ,²⁰ but it has since been reported¹² that the compound was really of formula S_3F_4 . Although we have no information on the structure of these compounds, it seems very probable that, like S_2F_4 and S_2F_{10} , they can be written formally in terms of single S-S bonds, i.e., SF_3-SF_3 , and SF_3-SF_5 rather than $F_2S = SF_4$ and $SF_4 = SF_4$. Calculated S-S bond strengths for these compounds are given in Table 2.

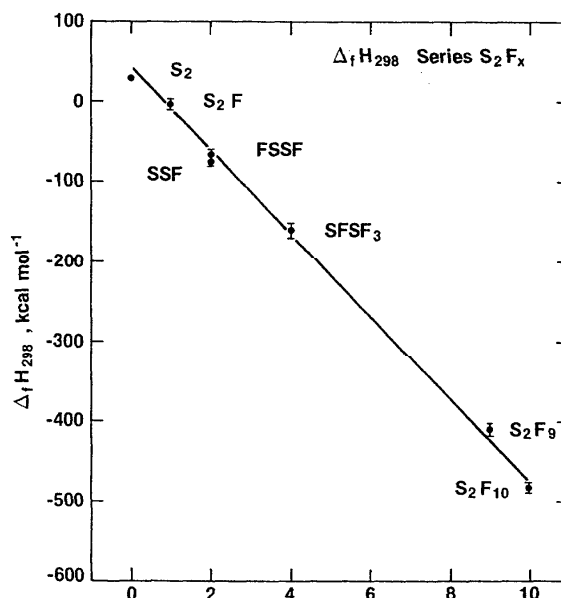


FIG. 2. $\Delta_f H_{298}^\circ$ for the series S_2F_x , $x = 0$ to 10.

5. Miscellaneous S-F-O Compounds

These are basically compounds containing the SF₅O or SF₅O₂ groups.

Czarnowski and Schumacher¹⁴ report $D^\circ(\text{SF}_5\text{O}-\text{OSF}_5) = 155.6 \text{ kJ mol}^{-1}$. Using $\Delta_f H^\circ(\text{SF}_5\text{O}) = -996 \pm 15 \text{ kJ mol}^{-1}$ from Table 1, $\Delta_f H^\circ(\text{SF}_5\text{O})_2 = -2148 \pm 25 \text{ kJ mol}^{-1}$.

The enthalpy of formation of SF₅O₂ may be estimated from the reported activation energy of 56.5 kJ mol^{-1} ,¹⁴ for the process SF₅O₂ → SF₅ + O₂, and auxiliary data from Table 1, i.e., $\Delta_f H^\circ(\text{SF}_5\text{O}_2) = -969 \pm 15 \text{ kJ mol}^{-1}$.

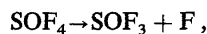
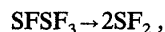
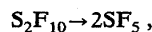
For SF₅O₃SF₅, the activation energy for the process SF₅O₃SF₅ → SF₅O + SF₅O₂ has been reported to be $105.9 \text{ kJ mol}^{-1}$.²² Using auxiliary data from Table 1, $\Delta_f H^\circ(\text{SF}_5\text{O}_3\text{SF}_5) = -2069 \pm 21 \text{ kJ mol}^{-1}$.

The activation energy of the reaction SF₅OF → SF₅O + F has been reported²³ to be 172 kJ mol^{-1} . Using data from Table 1, $\Delta_f H^\circ(\text{SF}_5\text{OF}) = -1089 \pm 15 \text{ kJ mol}^{-1}$. In considering these bond scission reactions, it has been assumed in every case that the activation energy of the reverse process is zero.

6. Summary and Conclusions

This review has provided, wherever possible, a consistent set of thermochemical data for use in modeling chemical processes involving SF₆ and its thermal and oxidative reaction products. The older data incorporated in the review of Benson¹ and the JANAF Tables²⁻⁵ have been reexamined, and new data available since those reviews appeared have been incorporated.

In order to put the estimation method used here on a more quantitative basis, however, reliable data are needed on the enthalpies of the reactions:



and independent measurements of enthalpies of formation of SOF₂ and SOF₄. There is a particularly strong need for a better measurement of $\Delta_f H^\circ(\text{SF}_4)$ which has an unacceptably large uncertainty of $\pm 21 \text{ kJ mol}^{-1}$. In addition, there is

some question as to the correct value for $\Delta_f H^\circ$ of SF₂.

In the case of the entropy data, the situation is somewhat better as there are spectroscopic and structural data available for many of the compounds of interest.

7. Acknowledgments

I wish to thank Professor H. Willner for providing a copy of his paper prior to publication. This work was supported by the Office of Standard Reference Data of the National Bureau of Standards.

8. References

- ¹S. W. Benson, *Chem. Rev.* **78**, 23 (1978).
- ²M. W. Chase, Jr., J. L. Curnett, J. R. Downey, Jr., R. A. McDonald, A. N. Syverud, and E. A. Valenzuela, *J. Phys. Chem. Ref. Data* **11**, 695 (1982).
- ³M. W. Chase, Jr., J. L. Curnett, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **7**, 793 (1978).
- ⁴M. W. Chase, Jr., J. L. Curnett, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data* **3**, 311 (1974).
- ⁵D. R. Stull and H. Prophet, *JANAF Thermochemical Tables, Second Edition* (U. S. GPO, Washington, D.C., 1971).
- ⁶K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides* (Butterworths, London, 1974).
- ⁷T. Kiang and R. N. Zare, *J. Am. Chem. Soc.* **102**, 4024 (1980).
- ⁸J. L. Lyman, *J. Chem. Phys.* **67**, 1868 (1977).
- ⁹J. F. Bott and T. A. Jacobs, *J. Chem. Phys.* **50**, 3850 (1969).
- ¹⁰J. F. Bott, *J. Chem. Phys.* **54**, 181 (1971).
- ¹¹D. L. Hildebrand, *J. Phys. Chem.* **77**, 897 (1973).
- ¹²O. Lösking, H. Willner, H. Baumgärtel, H. W. Jochims, and E. Rühl, *Z. Anorg. Allg. Chem.* **530**, 169 (1985).
- ¹³R. D. Levin and S. G. Lias, "Ionization and Appearance Potential Measurements, 1971-1981," NSRDS-NBS 71 (U. S. GPO, Washington, D.C., 1982).
- ¹⁴J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kin.* **10**, 111 (1978).
- ¹⁵K. L. Wray and E. V. Feldman, *J. Chem. Phys.* **54**, 3445 (1971).
- ¹⁶H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data Suppl.* **6** (1977).
- ¹⁷W. Gombler, A. Haas, and H. Willner, *Z. Anorg. Allg. Chem.* **469**, 135 (1980).
- ¹⁸S. W. Benson and J. Bott, *Int. J. Chem. Kin.* **1**, 451 (1969).
- ¹⁹J. T. Herron, *Int. J. Chem. Kinetics* (to be published).
- ²⁰H. Willner, *J. Fluorine Chem.* **23**, 466 (1983).
- ²¹M. Feliz and H. J. Schumacher, *J. Photochem.* **15**, 109 (1981).
- ²²J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kin.* **11**, 1089 (1979).
- ²³A. J. Colussi and H. J. Schumacher, *Z. Phys. Chem. N. F.* **78**, 257 (1972).
- ²⁴K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta Part A* **33**, 323 (1977).