Thermochimica Acta, 235 (1994) 277–279
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01545-E

Note

Ideal gas state thermodynamic functions for perfluoro-2-aza-propene (CF_3–N=CF_2)

H. Aleman and J. Lielmezs *

Department of Chemical Engineering, The University of British Columbia, Vancouver, B.C. V6T 1Z4 (Canada)

(Received 30 June 1993; accepted 7 August 1993)

Abstract

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) have been calculated for perfluoro-2-aza-propene (CF_3–N=CF_2) in the ideal gas state from 298.15 to 1200 K at 1 bar pressure.

DISCUSSION

The ideal gas state thermodynamic functions, heat capacity, enthalpy, entropy and free energy, for perfluoro-2-aza-propene (CF_3–N=CF_2) have been calculated from 298.15 to 1200 K at 1 bar pressure by means of the commonly used statistical methods, treating the internal rotational barrier contribution by the method of Pitzer [1]. The vibrational frequency assignments, the internal rotational barrier height and other structural data needed to calculate the reduced moments of inertia were taken from the work of Trepalin et al. [2] while the value of the normal boiling point temperature was taken from the Haas-Gmelin Handbook of Inorganic Chemistry [3].

The results obtained are listed in Table 1. The functions have been fitted to a five-constant polynomial as

$$\Lambda = a + bT + cT^2 + dT^3 + eT^4 \tag{1}$$

where Λ is any thermodynamic function at temperature T (in K). The constants a, b, c, d and e (eqn. (1)) were calculated using linear least-squares curve-fitting methods, and are listed in Table 2. Table 3 lists the molecular data used for the calculation of the thermodynamic functions.

If we consider the overall reliability of the used spectroscopic and structural data (Table 3), we estimate the calculated thermodynamic function accuracy to be within ±3%, i.e. within the experimental error range.

---

* Corresponding author.

0040-6031/94/$07.00 © 1994 – Elsevier Science B.V. All rights reserved

TABLE 1

Ideal gas state thermodynamic functions of CF_3–N=CF_2

Temperature in K	$C_p^\ominus$ in J mol^{-1} K^{-1};	$(H^\ominus - H_0^\ominus)/T$ in J mol^{-1} K^{-1}	$-(F^\ominus - H_0^\ominus)/T$ in J mol^{-1} K^{-1}	$S^\ominus$ in J mol^{-1} K^{-1}
298.15	111.35	76.16	299.93	376.08
300.00	111.69	76.37	300.40	376.77
350.00	120.58	82.05	312.62	394.67
400.00	128.39	87.36	323.93	411.29
450.00	135.20	92.30	334.51	426.81
500.00	141.11	96.92	344.47	441.38
550.00	146.24	101.14	353.93	455.06
600.00	150.67	105.07	362.90	467.98
650.00	154.49	108.73	371.46	480.19
700.00	157.80	112.14	379.64	491.77
750.00	160.67	115.30	387.47	502.77
800.00	163.19	118.21	395.01	513.22
850.00	165.39	120.92	402.26	523.18
900.00	167.31	123.45	409.24	532.69
950.00	169.01	125.80	415.97	541.78
1000.00	170.51	128.00	422.48	550.48
1050.00	171.84	130.05	428.78	558.83
1100.00	173.02	131.98	434.87	566.85
1150.00	174.07	133.79	440.77	574.57
1200.00	175.01	135.49	446.50	582.00

This is corroborated by Table 4 which presents uncertainties calculated in $C_p^\ominus$ and $S^\ominus$ values at temperatures of 298.15 and 1200 K if the five lowest-valued frequencies are changed by ±10 and ±20%. As expected the %-*e* error in calculation decreases with increase in temperature (Table 4).

ACKNOWLEDGMENT

The financial assistance of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

TABLE 2

Calculated constants *a*, *b*, *c*, *d* and *e* in eqn. (1); all values in J mol^{-1} K^{-1}

	a	b	$c \times 10^3$	$d \times 10^6$	$e \times 10^{10}$
$C_p^\ominus$	26.768	0.39446	−0.43886	0.24096	−0.52819
$(H^\ominus - H_0^\ominus)/T$	32.365	0.17841	−0.11709	0.03907	−0.04758
$-(F^\ominus - H_0^\ominus)/T$	206.45	0.38936	−0.30017	0.16792	−0.41056
$S^\ominus$	238.81	0.56775	−0.41721	0.20691	−0.45776

TABLE 3

Fundamental frequencies and molecular structural data used

Fundamental frequencies ν m^{-1} [2]
1806.50, 1334.20, 1298.70, 1275.40, 1207.10, 1004.40, 852.00, 726.00, 632.30, 620.00, 544.60, 543.00, 444.60, 421.20, 368.50, 155.40, 151.80, 48.10

Internal rotational barrier	516 cm^{-1}	[2]
Product of principal moment of inertia	101849×10^{-117} g^3 cm^6	this work
Reduced moment of inertia	50.34×10^{-40} g cm^2	this work
Bond lengths and structural angles		[2]
Symmetry number	1	
Number of minima per revolution of top	3	
Molecular weight	133.030 kg mol^{-1}	[3]
Normal boiling point	240.0 K	[3]
Pressure	1 bar	

TABLE 4

Uncertainties in $C_p^\ominus$ and $S^\ominus$ values at 298.15 and 1200 K if the five lowest-valued frequencies (Table 3) are changed by ±10% and ±20%

Function	Temperature in K	Uncertainty in %			
		+10%	+20%	−10%	−20%
$C_p^\ominus$	298.15	−0.79	−1.59	+0.75	+1.46
	1200.00	−0.04	−0.09	+0.04	+0.07
$S^\ominus$	298.15	−0.91	−1.73	+0.77	+2.22
	1200.00	−0.67	−1.29	+0.75	+1.58

REFERENCES

1 K.S. Pitzer, Quantum Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1953.

2 S.V. Trepalin, A.Yu. Aksinenko and A.F. Gontarov, Russ. J. Phys. Chem., 63 (1989) 1449.

3 A. Haas-Gmelin, Handbook of Inorganic Chemistry, Part 9, Springer-Verlag, New York, 1981, pp. 125, 137.