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THEORETICAL THERMOCHEMISTRY: ENTROPIES AND HEAT CAPACITIES FOR A SERIES OF ORGANOSILICON COMPOUNDS. PART I

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ABSTRACT

Ab initio molecular orbital theory is used to compute entropies and heat capacities for SiH_2, SiH_4, CH_3SiH_3, $H_2Si{=}CH_2$ and $H_2Si{=}SiH_2$ in the temperature range 300–1500 K. In order to illustrate the reliability of our calculations we have included computations for H_2 and CH_4 for which precise experimental data exist. For H_2 and CH_4, the maximum deviation of our calculated entropies and heat capacities compared with the known values is about 1 J K^{-1} mol^{-1}, but for the series of organosilicon compounds for which precise thermodynamic data are often lacking, we can only compare some of our results with the literature values we have found; they are also consistent with our calculations with a maximum deviation of about 2 J K^{-1} mol^{-1} at lower temperatures and 1 e.u. at higher ones, whether they derive from experiments, statistical mechanics or empirical estimations. Furthermore, on the basis of all the above calculated heat capacity results for all the compounds involved, we have fitted the temperature-dependent functions for the heat capacities in the forms $(a + bT + cT^2)$ and $(a' + b'T + c'T^{-2})$ in the 300–1500 K range, and have found that the former fitting form for which our maximum fitting square deviations are less than 2 J K^{-1} mol^{-1} is better than the latter for all the calculated species; for H_2 and CH_4, all our fitting results are close to the literature values. Finally, although the present ab initio method is still subject to great uncertainties for the calculation of the absolute electronic energies, it is reasonable and practical, in a sense, for it to be used to calculate the entropy and heat capacity. Thus, a new way of determining thermodynamic data can be derived and is expected to be established.

INTRODUCTION

The concept of "theoretical thermochemistry" was first proposed in 1985 by Pople et al. [1], who calculated heats of formation of AH_m molecules [1], and ionization energies and proton affinities of AH_n molecules [2] based on the ab initio calculation. They pointed out that, "The time now seems ripe to exploit this new capability (the techniques of ab initio calculations) for systematic prediction of thermodynamic properties [1]", but research on this subject is still in its early stages and so far we have not seen a specific report concerning the purely theoretical calculation of entropy and heat capacity.

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Recently, a large number of organosilicon compounds have been widely studied, both in theory and in practice, because of their widespread importance [3,4]. We have also been interested in the part of the organosilicon compounds which contains the Si=Si and Si=C double bonds [5,6]. In our present work, we have selected several organosilicon compounds of great importance in organosilicon chemistry and have calculated their thermodynamic properties. Although our purpose has been to establish thermodynamic data for some organosilicons, we hope even more that what we have done will be helpful in establishing a new method for obtaining thermodynamic data, that is, the purely theoretical method based on the ab initio calculation. Of course, there are many practical and precise methods that have been established by chemists: the experimental measurement of heat; the statistical mechanical method based on spectroscopy [7,8,9]; and the empirical estimation method which was first established by Benson and Robin [10,11]. We hope that this kind of theoretical calculation can provide supplementary contributions to thermochemistry by exploiting its characteristic advantages.

COMPUTATIONAL METHODS

Quantum-chemical calculations were carried out using the well-known ab initio SCF calculations. Entropy and heat capacity were calculated according to the general statistical thermodynamic method [12]. The absolute entropy of the ideal gas at 1 atm can be written

$$S^{\ominus} = S_t^{\ominus} + S_r^{\ominus} + S_v^{\ominus} \qquad (1)$$

where $S_t^{\ominus}$, $S_r^{\ominus}$ and $S_v^{\ominus}$ are the translational, rotational and vibrational entropies, respectively, and according to statistical thermodynamics, they follow

$$S_t^{\ominus} = R\ \ln(f_t e/N_0) + 1.5R \qquad (2)$$

where f_t is the translational molecular partition function which depends on the mass of the molecule and the temperature, N_0 is Avogadro's constant and R is the gas constant.

$$S_r^{\ominus} = R\ \ln(f_r) + 1.5R \text{ (for a non-linear molecule)}$$

$$S_r^{\ominus} = R\ \ln(f_r + R) \text{ (for a linear molecule)} \qquad (3)$$

where f_r is the rotational molecular partition function which depends on the molecular mass and the optimised molecular geometric configurations and

$$S_v^{\ominus} = R\ \ln(f_v) + U_v^{\ominus}/T \qquad (4)$$

where f_v is the sum of various harmonic vibrational partition functions and $U_v^{\ominus}$ is the sum of various harmonic vibrational energies, both of which depend on all the harmonic vibrational frequencies calculated with the IMSPAK program.

The heat capacity at 1 atm can be written as

$$C_p^{\ominus} = C_t^{\ominus} + C_v^{\ominus} + C_r^{\ominus} + R \tag{5}$$

where $C_t^{\ominus}$ is the contribution of the translation, $C_r^{\ominus}$ is the rotation contribution and $C_v^{\ominus}$ is the vibration contribution which mainly depends on various harmonic frequencies.

The calculation of the numerical values was completed using the epidemic GAUSSIAN-80 program and the optimization of the equilibrium geometrical configuration was performed using the 3-21G basis set. IMSPAK programs were used to calculate the harmonic vibrational frequencies of various substances. All the above computations were carried out on the FACOM-M340S machine at Shangdong University.

In addition, the calculation of the entropy and heat capacity, and the fitting of the temperature-dependent function for heat capacity were completed using self-compiled programs on the HP9816 microcomputer of our Institute.

RESULTS AND DISCUSSION

Configurations and frequencies

All the optimized molecular configurations involved are given in Fig. 1 and the various vibrational frequencies are listed in Table 1.

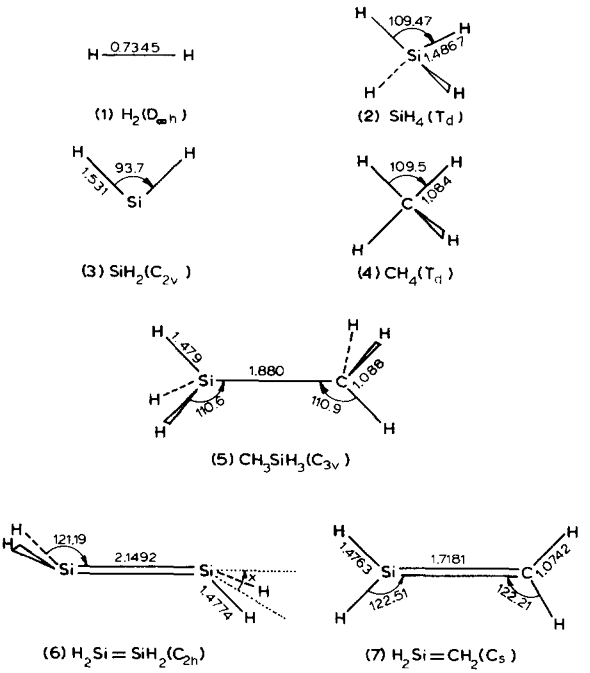
The sample compounds: H_2 and CH_4

Although these two compounds do not belong to the organosilicon series, the same level of theoretical calculation was applied to them in order to illustrate the reliability of our calculational method by comparison with established literature values. This is because the present theoretical methods are far from perfect and it is difficult to estimate the precise errors involved.

The entropy and heat capacity at different temperatures

The calculated and literature values for H_2 are listed in Table 2. Compared with ref. 13, our calculated $S^{\ominus}$ values are lower by an average of 0.59 J K^{-1} mol^{-1} with a maximum deviation of about 0.75 J K^{-1} mol^{-1}, and our $C_p^{\ominus}$ values are lower by an average of 0.25 J K^{-1} mol^{-1} with a maximum deviation of about 0.65 J K^{-1} mol^{-1}. The deviation increases gradually with increasing temperature.

Similarly, those of CH_4 are listed in Table 3. Compared with ref. 13, our calculated $S^{\ominus}$ values are lower by an average of 0.87 J K^{-1} mol^{-1} with a



(1) $H_2(D_{\infty h})$

(2) $SiH_4(T_d)$

(3) $SiH_2(C_{2v})$

(4) $CH_4(T_d)$

(5) $CH_3SiH_3(C_{3v})$

(6) $H_2Si=SiH_2(C_{2h})$

(7) $H_2Si=CH_2(C_s)$

Fig. 1. Configurations for every species involved. Bond lengths in Å, angles in deg. $X = 15.66$ (angle between Si–Si axis and Si–H–H plane).

maximum deviation of about 1.24 J K^{-1} mol^{-1}, and our $C_p^{\ominus}$ values are lower by an average of 0.66 J K^{-1} mol^{-1} with a maximum deviation of about 0.75 J K^{-1} mol^{-1}. The deviation increases gradually with increasing temperature.

TABLE 1

The harmonic vibrational frequencies (cm^{-1})

$H_2(D_{\infty h})$:	4672						
$CH_4(T_d)$:	1355.0	1355	1357	1548	1549	2819	2906
	2911.0	2923					
$SiH_4(T_d)$:	972.2	974.3	974.7	1046	1047	2276	2283
	2289	2303					
$SiH_2(C_{2v})$:	984.3	2024	2062				
$CH_3SiH_3(C_{3v})$:	266.6	511.6	513.8	689.8	885.6	903.3	
	904.2	915.8	916.7	1336.0	1459.0	1461.0	
	2060	2067	2078	2822	2884	2901	
$H_2SiSiH_2(C_{2h})$:	2360	2350	2340	2303	993.8	921.7	
	623.6	612.5	601.7	587.3	407.1	302.1	
$H_2CSiH_2(C_s)$:	3420	3324	2356	2346	1559	1043	
	980.8	963.5	952.4	820.1	561.1	542.3	

TABLE 2

The $C_p^\ominus$ and $S^\ominus$ (J K^{-1} mol^{-1}) values for H_2

T	$S^\ominus$		$C_p^\ominus$	
	a	b	a	b
300	130.25	130.76	29.10	28.85
400	138.63	139.12	29.10	29.18
500	145.12	145.64	29.10	29.26
600	150.43	150.98	29.11	29.32
700	154.92	155.51	29.15	29.43
800	158.81	159.44	29.23	29.61
900	162.26	162.95	29.36	29.87
1000	165.37	166.12	29.55	30.20
1100	168.19		29.79	
1200	170.8		30.07	
1300	173.22		30.38	
1400	175.48		30.70	
1500	177.61		31.03	

[a] From the present work.

[b] From ref. 13.

In general, the maximum deviation of our calculated entropy and heat capacity values for H_2 and CH_4 is about 1 J K^{-1} mol^{-1}. Therefore, our theoretical scheme is satisfactory. Furthermore, almost all our calculated values are lower than the literature values. We believe that this is because of

TABLE 3

The $C_p^\ominus$ and $S^\ominus$ (J K^{-1} mol^{-1}) values for CH_4

T	$S^\ominus$		$C_p^\ominus$	
	a	b	a	b
300	186.13	186.52	35.40	35.77
400	196.88	197.44	39.94	40.63
500	206.41	207.15	45.74	46.53
600	215.28	216.15	51.75	52.51
700	223.7	224.68	57.53	58.20
800	231.73	232.80	62.87	63.51
900	239.42	240.58	67.72	68.37
1000	246.79	248.03	72.05	72.80
1100	253.84		75.88	
1200	260.59		79.25	
1300	267.05		82.20	
1400	273.24		84.77	
1500	279.17		87.03	

[a] From the present work.

[b] From ref. 13.

TABLE 4

The fitting parameters for CH_4 and H_2

	H_2			CH_4		
	[a]	[b]	[c]	[a]	[b]	[d]
a ($J\,K^{-1}\,mol^{-1}$)	29.5309	29.0658	28.7859	12.4275	14.1461	23.64
b ($J\,K^{-2}\,mol^{-1}$) (-3)	-1.9060	-0.8364	0.2761	77.6799	75.496	47.9
c ($J\,K^{-3}\,mol^{-1}$) (-6)	1.9498	2.0117	1.1673	-18.4856	-17.9912	-19.3
S [f]	0.00083			0.4495		
	[a]	[e]	[c]	[a]	[e]	[c]
a ($J\,K^{-1}\,mol^{-1}$)	27.2829	27.28	27.280	32.6898	23.64	14.318
b ($J\,K^{-2}\,mol^{-1}$) (-3)	2.3279	3.26	3.264	38.3479	47.86	74.663
c ($J\,K^{-3}\,mol^{-1}$) ($+6$)	0.1140	0.050	0.0502	-0.9540	-0.192	1.7426
S [f]	0.02766			4.0106		

[a] From the present work; temperature range 300–1500 K.

[b] From ref. 14; temperature range 300–1500 K.

[c] From ref. 15; temperature range 273–2500 K for the first form for H_2; 298–3000 K for the second form for H_2; 291–1500 K for CH_4.

[d] From ref. 17; temperature range 298–2000 K.

[e] From ref. 16; temperature range 298–2000 K.

[f] The fitting square deviation.

the anharmonicity, the interaction between vibration and rotation, which we have not taken into account.

The fitting of the heat capacity

The fitting results in the form of both $(a + bT + cT^2)$ and $(a' + b'T + c'T^{-2})$ for H_2 and CH_4 are gathered in Table 4. It can be seen that most our fitting results agree with the literature values. For the first form, for H_2, our result is near to those of both refs. 14 and 15, and for the second form, our result basically agrees with those of both refs. 15 and 16 which have broader temperature ranges than ours.

However, for the first form for CH_4, our result approaches that of ref. 14 but is further from that of ref. 17. Therefore, we think that ref. 14 has the better result. For the second form for CH_4, there are greater apparent differences between our results and those of refs. 15 and 16. We think that this is mainly because the form $(a' + b'T + c'T^{-2})$ is worse for fitting the heat capacity of CH_4, as can be seen from the high value of the fitting square deviation ($S = 4.0106$). It will be shown in the next section on the derived thermodynamic data that in spite of their apparent differences, all the derived results are near to each other and to the literature values at different temperatures.

The derived thermodynamic data

In order to further demonstrate the reliability of our fitting results and to show what can be obtained from the fitting functions of the heat capacity,

TABLE 5

The derived thermodynamic data for CH_4

Functions		Temperature (K)							
		300	400	500	600	700	800	900	1000
$C_p^{\ominus}$	a	35.77	40.63	46.53	52.51	58.20	63.51	68.37	72.80
($J\ K^{-1}\ mol^{-1}$)	b	35.87	41.58	46.80	51.82	56.75	61.63	66.48	71.31
	c	34.07	40.54	46.65	52.38	57.75	62.74	67.37	71.62
	d	35.73	42.07	48.05	53.05	57.59	61.88	66.03	70.08
$S^{\ominus}$	a	186.52	197.44	207.15	216.15	224.68	232.80	240.58	248.03
($J\ K^{-1}\ mol^{-1}$)	b		197.64	207.49	216.46	224.82	232.72	240.26	247.51
	c		197.22	206.93	215.94	224.43	232.47	240.13	247.45
	d		197.44	207.50	216.71	225.23	233.20	240.73	247.90
$H_T^{\ominus} - H_{298}^{\ominus}$	a		3.89	8.24	13.22	18.74	24.85	31.42	38.49
($kJ\ mol^{-1}$)	b		3.88	8.30	13.23	18.66	24.58	30.99	37.88
	c		3.73	8.10	13.05	18.56	24.59	31.10	38.05
	d		3.82	8.33	13.39	18.93	24.90	31.30	38.11

[a] From the tabulated values in ref. 13.

[b] From the fitting parameters in ref. 16.

[c] From the fitting parameters of the first form of our work.

[d] From the fitting parameters of the second form of our work.

we have derived $C_p^{\ominus}$, $S^{\ominus}$ and $H_T^{\ominus} - H_{298}^{\ominus}$ from the fittings of our results and the literature values [16] for CH_4, and have listed them in Table 5 where they are compared with the experimental values [13].

Firstly, we can see from the various thermodynamic values in Table 5 that, compared with ref. 13, the fitting of ref. 16 is not as good as our fitting with the first form, but that it is on average better than our fitting with the second form. Of course, all the differences between them are not great.

Secondly, for the second fitting form for CH_4 with $S = 4.0106$ which is the worst of all the above fittings, the maximum deviations compared with those of ref. 13 are about 2 $J\ K^{-1}\ mol^{-1}$ for $C_p^{\ominus}$, 1 $J\ K^{-1}\ mol^{-1}$ for $S^{\ominus}$ and 0.5 $kJ\ mol^{-1}$ for $H_T - H_{298}$. Therefore, in view of the maximum calculated error of about 1 $J\ K^{-1}\ mol^{-1}$ for H_2 and CH_4, we feel that our fittings with fitting square deviations less than 0.5 are satisfactory.

The series of organosilicon compounds

All the calculated entropies and heat capacities, and the corresponding literature values, are listed in Table 6; the fitting results are in Table 7.

SiH_4

Silane is the most important compound in organosilicon chemistry and precise experimental data exist for it. In 1955, Altschuler [18] calculated entropies and heat capacities at different temperatures for SiH_4 according to

TABLE 6

The $S^\ominus$ and $C_p^\ominus$ values of a series of organosilicon compounds (J K^{-1} mol^{-1})

Compounds			Temperature (K)							
			300	400	500	600	700	800	900	1000
SiH_4	$S^\ominus$	a	204.27	217.27	229.11	240.1	250.37	260.0	269.06	277.59
		b	204.51	218.32	230.40	242.0	252.59	262.5	271.8	280.54
	$C_p^\ominus$	a	41.33	49.38	56.94	63.67	69.57	74.68	79.05	82.76
		b	42.76	51.42	59.08	65.81	71.67	76.65	80.88	84.47
SiH_2	$S^\ominus$	a	207.73	218.07	226.58	233.95	240.53	246.51	251.99	257.05
		c	207.44	217.78	226.31	233.68	240.29	246.27	251.79	
	$C_p^\ominus$	a	35.03	37.04	39.31	41.61	43.77	45.70	47.37	48.78
CH_3SiH_3	$S^\ominus$	a	253.75	275.02	294.81	313.26	330.52	346.69	361.87	376.15
		d	252.00							
	$C_p^\ominus$	a	66.31	81.99	95.48	107.0	116.84	125.27	132.46	138.6
		d	66.11		98.80			120.67		133.47
$H_2Si{=}CH_2$	$S^\ominus$	a	239.92	255.31	269.39	282.35	294.33	305.47	315.86	325.62
	$C_p^\ominus$	a	48.58	58.75	67.48	74.69	80.75	85.98	90.58	94.66
$H_2Si{=}SiH_2$	$S^\ominus$	a	265.39	286.26	304.47	320.61	335.15	348.4	360.6	371.9
	$C_p^\ominus$	a	67.24	77.73	85.42	91.65	96.97	101.57	105.54	108.94

[a] From the present work.

[b] From ref. 18.

[c] From ref. 19.

[d] From ref. 20.

the spectroscopic data and the data in Table 6 show that they agree well with our results. The deviations for $S^\ominus$ and $C_p^\ominus$ are less than 0.5 J K^{-1} mol^{-1} at 300 K and less than 3 J K^{-1} mol^{-1} at all other temperatures. In 1966, O'Neal and Ring [21] estimated $S^\ominus$ to be about 208.61 J K^{-1} mol^{-1} and C_p to be about 37.66 J K^{-1} mol^{-1} at 298.17 K for SiH_4 by the method of additivity rules which has errors of more than 1 e.u. for both $S^\ominus$ and $C_p^\ominus$

TABLE 7

The fitting parameters for the heat capacity of a series of organosilicon compounds [a]

Parameters	SiH_4	SiH_2	CH_3SiH_3	$H_2Si{=}CH_2$	$H_2Si{=}SiH_2$
a (J K^{-1} mol^{-1})	14.8033	25.9316	21.1271	21.2263	42.2383
b (J K^{-2} mol^{-1}) (−3)	99.4154	31.9041	174.2983	106.4777	100.2205
c (J K^{-3} mol^{-1}) (−6)	−31.2432	−9.1704	−56.0415	−32.3696	−32.8732
S [b]	0.2425	0.03592	1.9053	1.1210	1.3216
a (J K^{-1} mol^{-1})	52.0569	36.3242	89.2048	61.1093	82.9799
b (J K^{-2} mol^{-1}) (−3)	30.6260	12.1300	49.9441	34.2190	26.6544
c (J K^{-3} mol^{-1}) (+6)	−1.9766	−0.5145	−3.6975	−2.2036	−2.2668
S [b]	4.6120	0.7313	11.0751	2.8709	2.5493

[a] The temperature range is 300–1500 K.

[b] S is the fitting square deviation.

compared with ref. 18. From Table 7 we can see that the first fitting form is better, with $S = 0.2425$ which is very satisfactory, compared with the second form which is not, with $S = 4.162$.

SiH_2

This widely studied substance is used as an important intermediate [3] in organosilicon chemistry, and discussion concerning its enthalpy of formation, both experimental and theoretical, has been extensive [3]. Table 6 lists its entropy values calculated by John and Purnell in 1971 [19] on the basis of spectroscopic data with a deviation of about ±1 e.u.; they are almost the same as ours, with the maximum difference being less than 0.3 J K^{-1} mol^{-1}. Bowrey and Purnell [22] have also obtained an $S^{\ominus}$ value for SiH_2 at 300 K of 207.11 J K^{-1} mol^{-1}, consistent with our results and with that in ref. 19. Furthermore, both fitting forms are satisfactory for SiH_2 with S and $S' < 1$ (see Table 7), the first form being better.

CH_3–SiH_3

This is a significant organosilicon compound which is used as an important intermediate in organic syntheses [23] and in many high-temperature reactions of organosilicons [24]. However, precise thermodynamic data are not available for it because it is a complex compound. In 1981, O'Neal and Runy [20] first established an estimation system suitable for some large saturated organosilicon compounds, and their estimations for the entropy and heat capacity of CH_3SiH_3 are very near to ours at 300 K with a deviation of less than 2 J K^{-1} mol^{-1}, see Table 6. At 1000 K, we obtained a deviation of about 5.13 J K^{-1} mol^{-1} for the heat capacity, but this is reasonable if O'Neal's suggested error of about ±1.0 e.u. is taken into account, and, of course, we feel that our results are preferable. The fitting results for CH_3–SiH_3 (Table 7) show that the first form is satisfactory with $S = 1.9 < 2$ whereas the second form with S about 11 should be rejected.

$H_2Si{=}CH_2$ and $H_2Si{=}SiH_2$

These are two basic organosilicon compounds containing a Si double bond, the research into which has recently rapidly developed, both in theory and in experiment [4,25]. However, there are so far no data for their $C_p^{\ominus}$ and $S^{\ominus}$ values because of their instability. Therefore, our calculations can provide meaningful predictions. For both of them, the first fitting results for heat capacity are preferable. Their fitting square deviations for both forms are near to each other being $S = 1.1210$ and $S = 1.3216$, and $S' = 2.8709$ and $S' = 2.5493$, respectively. This seems to suggest that they have similar structures.

CONCLUSIONS

In spite of the approximations and uncertainties in the calculated absolute electronic energies for the ab initio method used, the work above shows that it is practical in a sense for this type of method to be used to predict the entropy and heat capacity of gas-phase compounds. The maximum calculated deviation of the entropy and heat capacity is less than 1 J K^{-1} mol^{-1} for H_2 and CH_4, and 1 e.u. for all other comparisons in the temperature range 300–1000 K. For the series of organosilicon compounds, we found a maximum deviation of less than 2 J K^{-1} mol^{-1} at lower temperatures, which is a little superior to Benson's estimation method which has an error of about ±1 e.u. [26].

The purely theoretical calculation has many advantages. Many experimental methods cannot easily be used to investigate temperature, entropy and transient species (such as intermediates and transition states), but these present no obstacle to the theoretical calculation. In addition, the systematic processing of the data by computer, facilitates the selection of the temperature, the fitting of the heat capacity, etc., for the theoretical calculation.

We have fitted the heat capacity of the above organosilicon compounds to two forms in the temperature range 300–1500 K, and have found that the first kind of fitting is much more satisfactory ($S < 2$) than the second. The $S^{\ominus}$, $H_T^{\ominus} - H_{298}^{\ominus}$ and $H_T^{\ominus} - H_0^{\ominus}$ values can be derived from the fitting functions of the heat capacities according to the formulae, $(\partial S^{\ominus}/\partial T)_p = C_p^{\ominus}/T$ and $(\partial H^{\ominus}/\partial T)_p = C_p^{\ominus}$, and the complete thermodynamic data can be obtained if the absolute energy, $U^{\ominus}$, also derived from ab initio calculation, is added. Of course, we have not calculated the $\Delta H_{f298}^{\ominus}$, as it is even more easy to obtain than $S^{\ominus}$ and $C_p^{\ominus}$ by experiment.

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