

ON THE CALCULATION OF STANDARD THERMODYNAMIC FUNCTIONS OF DIATOMIC MOLECULES IN SF₆ PLASMA¹⁾

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The work deals with problems of determining standard thermodynamic functions $C_p^0(T)$, $\Phi^0(T)$, $S^0(T)$, $H^0(T)$, $H^0(0)$ and $G^0(T)$ of some molecular components present in SF₆ plasma at temperatures above 6000 K. In the available foreign literature these functions have been published only up to a temperature of 6000 K, with the exception of molecular fluorine. For the calculation the approximate method of Mayer and Geppert-Mayer has been chosen. The results of the calculations are then compared with NBS data (USA) and with IVTAN data (USSR).

1. INTRODUCTION

Recently great attention has been paid to the use of single-pressure systems with intrinsic accumulated energy used for electric arc quenching [e.g. 1]. The dynamic phenomenon of the nozzle clogging and delogging due to the action of the electric arc is accompanied, in addition to the SF₆ dissociation into single components, also by the pressure rise in the arc quenching chamber. With the pressure rise in the system the dissociation processes are suppressed and that is why molecular components of the SF₆, S₂, F₂ type may be present in the SF₆ plasma even in the region of elevated temperatures. Published data have not considered the occurrence of the mentioned components at temperatures above 6000 K because the necessary input data (standard thermodynamic functions — STF) are published only up to the temperature 6000 K. In this work the calculation results of STF for temperatures above 6000 K are presented.

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II. METHOD OF CALCULATION

The standard thermodynamic functions in the state of an ideal gas can be determined by means of the particle partition function [2]

$$Q(T) = \sum_i G_i \exp\left(-\frac{E_i}{KT}\right). \quad (1)$$

For one mol of gas in the ground state the STF are connected with the partition function and its derivations through the relations:

$$S^0(T) = R \ln \frac{Q(T)}{N} + RT \frac{\ln Q(T)}{T} \quad (2)$$

$$\Phi^0(T) = R \ln \frac{Q(T)}{N} \quad (3)$$

$$C_p^0(T) = RT^2 \frac{1}{T^2} \ln \frac{Q(T)}{T} + 2RT \frac{\ln Q(T)}{T} \quad (4)$$

$$H^0(T) - H^0(0) = T(S^0(T) - \Phi^0(T)) \quad (5)$$

$$G^0(T) = H^0(0) - T\Phi^0(T) = H^0(T) - TS^0(T). \quad (6)$$

The partition function (1) can be expressed in the form

$$Q_{\text{tot}}(T) = Q_{\text{tr}} \cdot Q_{\text{int}}. \quad (7)$$

The translation part takes for the diatomic molecules the form

$$Q_{\text{tr}} = \left(-\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot \frac{MKT}{p} \quad (8)$$

and the internal part

$$Q_{\text{int}} = \sum_i g_i \exp\left(-\frac{\epsilon_i}{KT}\right) Q_{\text{rot vib}}^i. \quad (9)$$

$Q_{\text{rot vib}}^i$ involves the summation over the vibrational and rotational energy levels of the molecule.

The most precise results in the calculation of the partition function and STF can be achieved by means of the direct summation [3] of electronic, vibrational and rotational states. Because, however, the number of vibrational-rotational levels is very high, the calculation by this method is rather difficult.

From the approximate methods published the most widely used is the Mayer and Geppert-Mayer (MGM) method [2] which was also chosen for our calculation.

Table 1

Comparison of STF for C_2 according to various methods and input data

T 10^3 K	1	2	3	4	5	6
	$\Phi^0(T)$ J mol $^{-1}$ K $^{-1}$					
1	210.996	211.053	211.047	210.985	210.983	210.985
6	274.990	276.254	276.252	275.614	275.579	275.445
10	291.998	—	296.748	295.637	295.573	295.183
15	—	—	313.915	312.209	312.110	311.337
	$S^0(T)$ J mol $^{-1}$ K $^{-1}$					
1	244.444	244.567	244.566	244.404	244.397	244.396
6	310.064	315.390	315.393	314.046	313.579	313.539
10	323.408	—	337.977	335.678	335.544	334.380
15	—	—	357.496	354.008	353.802	352.257
	$C_p^0(T)$ J mol $^{-1}$ K $^{-1}$					
1	35.057	37.175	37.175	36.947	36.934	36.919
6	28.917	42.597	42.604	41.176	41.091	40.207
10	23.955	—	46.107	43.728	43.586	41.508
15	—	—	50.467	46.898	46.684	50.555

Rem.: 1 — calculation by direct summation method [3];
 2 — calculation by MGM method with consideration on the basic electron level [4];
 3–6 — calculation of USPE:
 3 — by the MGM method with consideration of ground level input data [4];
 4 — the same as in 3. input data [3];
 5 — the same as in 3. input data [5];
 6 — by MGM method with excited electron levels considered. input data [5].

tion of the internal partition function in equation (9) the summation can be substituted over rotational and vibrational levels, provided these have an infinite number, by integration and $Q_{rot,vib}$ can be expressed as a simple explicit function of temperature and tabulated rotational-vibrational constants

$$Q_{rot,vib} = \frac{q_0}{\sigma(1 - e^{-u})} \left(1 + \frac{1}{3q_0} + d_0 + \frac{\beta_1}{e^v - 1} + \frac{2xu}{(e^v - 1)^2} \right). \quad (10)$$

β_1 , x , u , q_0 depend on temperature and rotational-vibrational constants determined on the basis of the analysis of rotational and vibrational-rotational spectra of molecules and mentioned compendiously in a number of mono-graphs. In this paper data from Ref. [5] were used, with data [3] and [4] employed for the comparison of the effect of input data on the resulting STF. Owing to the fact that papers [4, 5] do not mention the values of rotational-vibrational constants for the SF molecule, data from [3] were used.

III. RESULTS AND DISCUSSION

Shown in Table 1 and in Fig. 1 is the comparison of STF values for F_2 according to various methods and input data. The most precise results are provided by the direct summation method (column 1) with the limitation of the

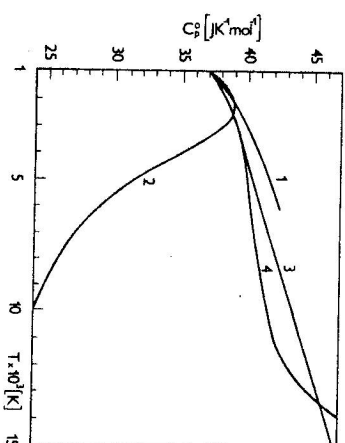


Fig. 1. Comparison of the temperature dependence $C_p^0(T)$. 1 — NBS 4; 2 — IVTAN [3]; 3 — USPE (ground state level); 4 — USPE (with all excited levels published)

particle partition function of vibrational-rotational energy levels. The calculation involves only the ground electronic state $X^1\Sigma_g^+$. The determined deviations at the temperature of 6000 K reach, in the case of the Φ^0 value 1.2 JK $^{-1}$ mol $^{-1}$, which itself in the calculation of the composition by changes in the molar

Table 2

Standard thermodynamic functions of F_2

T 10^3 K	$C_p^0(T)$ J K $^{-1}$ mol $^{-1}$	$\Phi^0(T)$ J K $^{-1}$ mol $^{-1}$	$H^0(T) - H^0(0)$ kJ mol $^{-1}$	$-(C_p^0(T) - H^0(0))$ kJ mol $^{-1}$
1.	36.918	244.396	210.985	33.411
2	38.266	270.491	234.924	71.135
3	38.913	286.138	249.556	109.745
4	39.409	297.402	260.174	148.914
5	39.832	306.428	268.535	188.539
6	40.207	313.539	275.445	228.562
7	40.544	319.762	281.342	268.940
8	40.853	325.197	286.492	309.640
9	41.156	330.026	291.066	350.644
10	41.508	334.380	295.183	391.969
11	42.022	338.358	298.929	433.714
12	42.891	342.048	302.371	476.130
13	44.385	345.535	305.558	519.703
14	46.831	348.907	308.534	565.218
15	50.555	352.257	311.337	613.792

Table 3

Standard thermodynamic functions of S ₂					
T 10 ³ K	C _p ⁰ (T)	S ⁰ (T) JK ⁻¹ mol ⁻¹	Φ ⁰ (T)	H ⁰ (T) - H ⁰ (0) kJ mol ⁻¹	-(G ⁰ (T) - H ⁰ (0)) kJ mol ⁻¹
1	37.265	270.660	236.667	33.992	236.667
2	40.117	297.412	261.035	72.756	522.069
3	41.579	313.999	276.095	113.711	828.285
4	42.571	326.089	287.149	155.760	1148.594
5	44.255	335.752	295.933	199.098	1479.664
6	46.728	344.030	303.277	244.540	1819.643
7	49.502	351.442	309.634	292.653	2167.438
8	52.042	358.222	315.290	343.462	2522.318
9	53.999	364.472	320.412	396.540	2883.706
10	55.258	370.232	325.110	441.227	3251.098
11	55.866	375.532	329.456	506.838	3624.018
12	55.955	380.400	333.502	562.786	4002.019
13	55.674	384.870	337.284	618.625	4384.686
14	55.157	388.978	340.831	674.056	4771.638
15	54.508	392.762	344.169	728.896	5162.535

Table 4

Standard thermodynamic functions of SF ₆					
T 10 ³ K	C _p ⁰ (T)	S ⁰ (T) JK ⁻¹ mol ⁻¹	Φ ⁰ (T)	H ⁰ (T) - H ⁰ (0) kJ mol ⁻¹	-(G ⁰ (T) - H ⁰ (0)) kJ mol ⁻¹
1	36.899	269.822	236.202	33.619	236.202
2	37.949	295.797	260.221	71.153	520.442
3	38.442	311.283	274.829	109.361	824.487
4	38.943	322.407	285.397	148.041	1141.586
5	39.691	331.171	293.705	187.331	1468.524
6	40.757	338.497	300.576	227.530	1803.454
7	42.046	344.875	306.458	268.920	2145.205
8	43.398	350.578	311.622	311.643	2492.980
9	44.676	355.764	316.243	355.691	2846.190
10	45.786	360.531	320.437	400.938	3204.369
11	46.689	364.939	324.285	447.193	3567.132
12	47.379	369.032	327.845	494.245	3934.141
13	47.875	372.845	331.162	541.887	4305.102
14	48.205	376.406	334.268	589.940	4679.749
15	48.401	379.740	337.189	638.253	5057.840

fraction F₂ by about 10%. Noted for the highest differences is the C_p⁰. This is because C_p⁰ contains the second derivation of the partition function. With increasing temperature the differences increase and at 10000 K they reach for

the Φ⁰ values 3.2 JK⁻¹ mol⁻¹ and for the C_p⁰ 4.0 JK⁻¹ mol⁻¹. The use of different input data (see columns 3—5) leads, as against other methods of calculation, to approximately one order lower differences. As it is clear from the courses of C_p⁰ in Fig. 1, the MGM method approximates, when all the published excited levels are considered, to the data obtained by means of the direct summation better than the NBS data (column 2).

Shown numerically in Tables 2 to 4 are the results of STF calculations for F₂, S₂ and SF with the use of data [5], [5] and [3], resp., and the excited levels F₂: X¹Σ_g⁺, F¹Π_g, C¹Σ_g⁺, F³Π_g, D¹Σ_g⁺, E¹Σ_g⁺, h³Π_u, H¹Π_u, I¹Σ_g⁺, J¹Π_u; S₂: X³Σ_g⁻, a¹Δ_g, b¹Σ_g⁺, A³Δ_u, A³Σ_u⁺, B³Σ_u⁻, B³Π_g, f⁴Δ_u, C³Σ_u⁻, g¹Δ_u, D³Π_u; SF: X²Π_g, A²Π_g.

IV. CONCLUSION

The calculated STF F₂, S₂, SF by means of the MGM method with the help of the latest data are applicable to the calculation of the equilibrium composition of SF₆ plasma for temperatures above 6000 K. The determined deviations in STF, in comparison with the direct summation method (with respect to their molar representation in plasma SF₆) are acceptable.

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К РАСЧЕТУ СТАНДАРТНЫХ ТЕРМОДИНАМИЧЕСКИХ ФУНКЦИЙ ДВУХАТОМНЫХ МОЛЕКУЛ В ПЛАЗМЕ SF₆

Работа посвящена проблеме определения стандартных термодинамических функций ствляющих в плазме SF₆ при температурах свыше 6000 К. В доступной зарубежной литературе эти функции, за исключением молекулы фтора, приводятся только до температуры 6000 К. Для расчетов был использован приближенный метод Майера и Геперт-Майер. Проведено сравнение результатов вычислений с данными НБС США и ИВТ АН СССР.