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Ab Initio Calculation of Molecular, Thermodynamic, and Kinetic Parameters of CF, CF_2, CF_3, and C_2F_5 Radicals and CF_4, CF_3I, C_2F_4, and C_2F_6 Molecules in Gas

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Abstract—Enthalpies of formation of ground states of the gaseous particles CF, CF_2, C_2F_5, CF_4, CF_3I, C_2F_4, and C_2F_6 were calculated by *ab initio* method in the CCSD(*T*) approximation with extrapolation to the full basis and regard to the correlation energy. Their equilibrium geometrics, frequencies of normal vibrations, and other values were found by the B3LYP/aug-cc-pvdz method, from which thermodynamic functions within the range of 0–6000 K were calculated. Equilibrium constants were calculated from these functions, and then the information on the rate constants in the limit of high pressures was obtained.

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Recently a discussion arises [1–3] concerning rate constants of reaction (1) of hexafluoroethane dissociation and the back reaction of the recombination of trifluoromethyl radicals.

$$C_2F_6\,(+M) \underset{k_{-1,M}}{\overset{k_{1,M}}{\rightleftharpoons}} 2\,CF_3^{\bullet}\,(+M) + \Delta_{r,1}H_T^0. \qquad (1)$$

Here the rate constants of direct and back reactions are interconnected through the equilibrium constant by relation (2).

$$K_{c,i}(T) = k_{1,M}/k_{-1,M} = A_{c,i}(T)\cdot e^{-\Delta_{r,i}H_0^0/RT},\ i = 1. \qquad (2)$$

In formula (2) $\Delta_{r,i}H_T^0$ is the change in the standard enthalpy of the reaction $i = 1$ at a temperature T; R is the gas constant; $A_{c,i}(T)$ is a preexponential factor with the dimension of a number of particles n, cm^{-3}.

The fundamental point of the disagreement between the authors of [1, 3] on the one hand and of [2], on the other, is the value of the enthalpy change in the process $\Delta_{r,i}H_0^0$, which was calculated in the works [1, 3] on the basis of the thermodynamic tables [4, 5], and in [2], from the more modern data [6]. Therefore the discussion is actually reduced to the check of correctness of the quantum-chemical calculations [6], which is the purpose of the present work.

As the revision of the thermochemistry of the particles C_2F_6, C_2F_5, and CF_3I will affect not only the energy of reaction (1), but also many other reactions, we shall touch upon the thermochemistry of several of such reactions (3)–(7), for which there are rather reliable experimental data.

$$C_2F_6\,(+M) \underset{k_{-3,M}}{\overset{k_{3,M}}{\rightleftharpoons}} C_2F_5^{\bullet} + F^{\bullet}\,(+M) + \Delta_{r,3}H_T^0, \qquad (3)$$

$$CF_4\,(+M) \underset{k_{-4,M}}{\overset{k_{4,M}}{\rightleftharpoons}} CF_3^{\bullet} + F^{\bullet}\,(+M) + \Delta_{r,4}H_T^0, \qquad (4)$$

$$CF_3I\,(+M) \underset{k_{-5,M}}{\overset{k_{5,M}}{\rightleftharpoons}} CF_3^{\bullet} + I^{\bullet}\,(+M) + \Delta_{r,5}H_T^0, \qquad (5)$$

$$C_2F_4\,(+M) \underset{k_{-6,M}}{\overset{k_{6,M}}{\rightleftharpoons}} 2\,CF_2^{\bullet}\,(+M) + \Delta_{r,6}H_T^0, \qquad (6)$$

$$CF_4\,(+M) \underset{k_{-7,M}}{\overset{k_{7,M}}{\rightleftharpoons}} CF_2^{\bullet} + F_2\,(+M) + \Delta_{r,7}H_T^0. \qquad (7)$$

The summary of thermochemical parameters for molecules under consideration is presented in Table 1. Enthalpy changes in reactions (1) and (3)–(7) calculated from the data of Table 1 are presented in Table 2. Only for reaction (5) the calculated enthalpy change can be considered as coinciding with the results

Table 1. Standard enthalpies of formation of some fluorine-containing molecules in gas phase, $\Delta_f H_T^0$, kJ mol^{-1}

Molecule (radical)	*T*, K	JANAF [7]	Reference data [4, 5]	Reference data [6]	Calculation by G2, G3, or G4	*Ab initio* calculation[a]
CF	0	251.6±9.0	240.5±10.0	258.2±4.5 [8]	243.3±0.8 [11] 242.9 [12]	245.3±2.0
	298	255.4±9.0	244.1±10.0	261.5±4.5 [8] 242.7[b]	247.0±0.8 [11]	249.3±2.0
CF_2	0	–182.5±6.5	–180.5±10.0		–193.6±1.2 [11]	–192.2±2.0
	298	–182.1±6.5	–180.0±10.0		–193.2±1.2 [11]	–190.5±2.0
CF_3	0	–467.7±4.2	–469.2±10.0	–462.8±2.0	–464.8±1.6 [11]	–464.7±1.6
	298	–470.6±4.2	–472.0±10.0	–465.6±2.0 –469.4[b]	–467.6±1.6 [11]	–465.8±1.6
C_2F_4	0	–655.6±3.0	–656.1±4.0			–664.3±4.0
	298	–659.0±3.0	–659.5±4.0	676.1[c] 679.1 [10]		–665.3±4.0
C_2F_5	0		–880.8±10.0			–880.3±4.0
	298	–891.2±5.5[d]	–896.0±10.0			–882.7±4.0
CF_4	0	–927.8±1.3	–927.2±3.0		–927.8±2.0 [11]	–929.1±2.0
	298	–933.8±1.3	–933.2±3.0	–936.8[b]	–933.8±2.0 [11] –931.7±2.8 [13] –931.5 [14]	–932.8±2.0
CF_3I	0	–583.6±3.5	–583.3±3.0	–580.3±2.2		–584.3±4.0
	298	–589.5±3.5	–589.2±3.0	–586.1±2.1		–587.6±4.0
C_2F_6	0	–1336±5	–1336±10	–1335.9±3.2		–1324.4±4.0
	298	–1345±5	–1344±10	–1344.2±3.2 –1351.0[c]	–1342.1±2.8 [13] –1348.5 [14]	–1328.9±4.0

[a] The error of our calculation is equal to the average deviation from the array of experimental data. Approximately a half of the error results from the uncertainty in the atomization energy of fluorine, therefore errors for different molecules have been correlated by ~50%. [b] *Ab initio* calculation at the G3 level. [c] Calculation at the G3 level with introduction of isodesmic correction. [d] Experimental data [9].

of measurements within the limits of errors. The value of $\Delta_{r,1}H_{300}^0$ for reaction (1), which we estimated at 401.7±4.0 kJ mol^{-1} on the basis of the measurements [15], agrees much better with the value of 397.5± 4.0 kJ mol^{-1}, which we have calculated, than with the value of 413.2±7.1 kJ mol^{-1} [6]. The principal reason of the discrepancy is the difference in the $\Delta_f H_T^0$ values for hexafluoroethane, which were calculated by us and by the authors of [6]. Furthermore, some distinctions are seen for the CF_3I molecule (Table 2). We shall consider this problem in more detail.

The quantum-chemical calculation of enthalpies of formation of the studied compounds was carried out by the CCSD(*T*) method with extrapolation to the complete (infinitely large) basis according to a scheme, which we have developed. The sequence of steps in the calculation is as follows.

(1) Optimization of the geometrical structure and the calculation of the vibration spectrum of a molecule, the energy of zero-point vibrations, and temperature corrections to the enthalpy and thermochemical parameters by the B3LYP method in the aug-cc-pvdz basis for carbon and fluorine (C, F basis). The SBD-aug-cc-pvtz basis [20] was used for the iodine atom. Scaling factors for vibration frequencies were not applied.

(2) Calculation of the total energy for the optimized structure by the CCSD and CCSD(*T*) methods in the aug-cc-pvNz basis (N = d, t, q) for carbon and fluorine and the SBD-aug-cc-pvtz fixed basis [20] for iodine.

(3) When it was impossible to fulfill a calculation by the CCSD(*T*) method in the aug-cc-pvqz basis because of the absence of convergence or of unacceptably high computer time expenditures, energy was estimated by taking into account triple excitations by formula (8).

$$E[CCSD(T),pvqz] = E(CCSD,pvqz) + \{E[CCSD(T),pvtz] - E(CCSD, pvtz\}/0.948. \quad (8)$$

Table 2. Increase in the enthalpy in gas-phase dissociation reactions (1)–(7), $\Delta_{f,i}H^0_T$, kJ mol^{-1}

Reaction, *i*	*T*, K	JANAF [7]	Reference data [4, 5]	Reference data [6]	*Ab initio* calculation[a]	Experimental data
(1)	0	401±14	397±30	410.6±7.2	395.0±4.0	
	298	404±14	400±30	413.2±7.2	397.3±4.0	401.7±4.0[c] [15]
(3)	0		532±20		521.4±4.0	
	298	531±11[b]	527±20	533±9[b]	525.6±4.0	523±4 [16]
(4)	0	537±7	535±13		541.7±2.0	539
	298	542±7	540±13	547±2	546.4±2.0	540±12 [16]
(5)	0	223±8	221±13	224.7±4.2	226.8±4.0	221±4[d]
						230±5[e]
	298	226±8	224±13	227.3±4.2	228.6±4.0	228±2 [19]
(6)	0	290±16	296±24		279.9±4.0	311±42 [16]
	298	295±16	300±24		284.3±4.0	316 [16]
(7)	0	745±8	747±13		736.9±4.0	
	298	752±8	753±13		742.3±4.0	

[a] Obtained from the data of the last column of Table 1. Errors were found in view of the 50% correlation of errors in our data in Table 1. [b] Calculated using $\Delta_f H^0(C_2F_5)$ from the work [9]. [c] Our estimate from the experimental data [15] within the limits of Gorin's model. [d] Approximating of the experimental data [17] by means of Kassel integral. [e] Calculation from the experimental data [18] by the Rice–Ramsperger–Kassel–Marcus theory.

Table 3. Geometrical parameters and principal moments of inertia optimized in the aug-cc-pvdz basis[a]

Parameter	$CF_2^{\cdot\cdot}$	$CF_3^{\cdot}$	CF_4	CF_3I	C_2F_4	$C_2F_5^{\cdot}$	C_2F_6
r(C–C)		–	–	–	1.3271	1.5189	1.5538
r(C–F)	1.3166	1.3300	1.3338	1.3430		1.3441	1.3417
r(C–I), *r*(C–F[b])			–	1.1585	1.3265	1.3296	–
φ(FCF)		111.295	109.2712	108.22		108.0	109.03
φ(FCF[b])	104.21		–	–	113.1	111.94	–
φ(FCI)			–	110.69		–	–
I_a	21.29813	169.39867	321.86604	321.26633	332.42220	489.69398	647.81135
I_b	146.4724	169.30867	321.86604	206.87913	565.68494	763.03287	995.33385
I_c	167.77053	327.19370	321.86604	206.87913	898.10715	928.58044	995.33385

[a] Measurement units: *r,* E, φ, deg, I_a, I_b, and I_c, au, [b] For the $CF_2^{\cdot\cdot}$ group.

(4) For each (C, F) aug-cc-pvNz (N = d, t, q) basis the enthalpy of formation under standard conditions was calculated. The following values of the heats of formation of atoms from elements (kJ mol^{-1}) were accepted [21]: 716.7 (C), 79.5 (F), and 106.8 (I).

(5) The extrapolation to the complete basis was carried out by three obtained values of the heat of formation on the assumption of exponential dependence (9) of the heat of formation on N (see point 2).

$$\Delta_f H(N) = \Delta_f H(CBS) + b\cdot\exp(-\alpha N). \quad (9)$$

Here N = 2 (pvDz), 3 (pvTz), and 4 (pvQz).

The calculated $\Delta_f H$(CBS) values for 298.15 and 0 K are presented in Table 1.

(6) For the $CF^{\cdot}$ radical the equilibrium C–F distance of 1.2902 E and three rotational moments were obtained: 0.0; 41.2814525; and 41.2814525 GHz (or: 0.0, 43.71797, and 43.71797 au). Molecular parameters for the remaining considered radicals and molecules are presented in Tables 3 and 4.

Calculated thermodynamic functions of the radicals $CF^{\cdot}$, $CF_2^{\cdot\cdot}$, $CF_3^{\cdot}$, $C_2F_5^{\cdot}$ and molecules CF_4, CF_3I, C_2F_4, and C_2F_6 (Tables 1 and Tables 5–12) allow us to obtain information on the rate constants of back reactions (1), (3)–(7), if rate constants of direct reactions are known and vice versa. Preexponential factor $A_{c,i}(T)$ in equilibrium constant (2) can be calculated from the values of the reduced Gibbs energy Φ^0 (Tables 5–12) by formula (10).

Table 4. Frequencies of normal vibrations (ν_i) for the main electronic states calculated theoretically (without using scaling factors)

Molecule, radical	Symmetry	ν_i, cm^{-1}
$CF^{\bullet}$	$C_{\infty v}$	1245.8
$CF_2^{\bullet}$	C_{2v}	650.8, 1064.1, 1189.5
$CF_3^{\bullet}$	C_{3v}	488.1 (2), 677, 1049.7, 1216.9 (2)
CF_4	T_d	415 (2), 604.7 (3), 881.7, 1229.6 (3)
CF_3I	C_{3v}	261 (2), 279.6, 517.4 (2), 721.6, 1039.8, 1143.5 (2)
C_2F_4	D_{2h}	197.1, 206.4, 389.4, 412.4, 540.2, 545.5, 551,6, 781.2, 1166.4, 1308.9, 1311.9, 1918.1
$C_2F_5^{\bullet}$	C_s	61.6, 204.8, 216.2, 356.4, 407, 496.3, 568.2, 590.9, 682, 799.4, 1085.1, 1147.8, 1188.8, 1250.4, 1387.1
C_2F_6	D_{3d}	61.4, 210.6 (2), 339.3, 367.1 (2), 502.3(2), 597.9 (2), 690.6, 784.8, 1087.8, 1189.9 (2), 1207 (2), 1385

$$A_{c,i}(T) = e^{-\Delta\Phi^{o}_{c,i}/R}. \quad (10)$$

Here $\Delta\Phi_{c,i}^{o}$ is a change of the reduced Gibbs energy in the *i*-th reaction on condition that the volume is constant. We shall calculate a preexponential factor for equilibrium (1) (Table 13, column 2), and then values of equilibrium constant (1) (Table 13, column 3). We start from the experimental data [15] processed within the limits of Gorin's model [22] for a transition complex. In the limit of high pressures we obtain formula (11) for the values of the rate constant $k_{1,\infty}$.

$$k_{1,\infty} = 10^{17.88}\exp[(-47510\pm500)/(T/K)]\ s^{-1}, \quad (11)$$
$$1300\text{–}1600\ K.$$

Now, using inverse formula (2*), we find the rate constant of recombination reaction (1) for the case *i* = 1 from the values of $k_{1,\infty}$ and $K_{c,1}$ (Table 13, column 5).

$$k_{-i,M} = k_{i,M}/K_{c,i}(T). \quad (2^*)$$

The rate constant $k_{-1,\infty}$ remains practically constant in a rather wide temperature range (from 1300 up to 1500 K) and equal to $10^{-0.6\pm0.1}$ cm^3 $molecule^{-1}$ s^{-1}. At the same time the experimental [3] value of $k_{-1,\infty}$(300 K) at room temperature is equal to $(1.27\pm0.05)\times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Thus, for the whole investigated range we obtain formula (12).

$$k_{-1,\infty}(300\text{–}1500\ K)$$
$$= 10^{-10.90\pm0.04}(T/300\ K)^{0.4\pm0.1}\ cm^3\ molecule^{-1}\ s^{-1}. \quad (12)$$

Temperature dependence (12) within the limits of errors agrees with the predictions of both Gorin's model $T^{1/6}$ [22] and Kondratyev's gas-kinetic model $T^{1/2}$ [23].

Values of $K_{c,1}$ from [2] presented in Table 13 (column 6) are based on the enthalpies of formation of hexafluoroethane and triflurомethyl radical calculated in [6]. However, the value of $k_{-1,\infty}(1300\ K) = 10^{-10.4}$ following from these data upon seaming with the value of $k_{-1,\infty}(300\ K)$ [3] results in the unreal too strong temperature dependence of $T^{0.8}$. Therefore, the enthalpy of formation of the molecule C_2F_6 found in [6] is contradictory to not only the measurings [15], but also the kinetic data [3], and, which is the most important, our quantum mechanical calculation (Table 1) does not confirm it.

The data of Table 13 show that the rate constant $k_{-1,\infty}$ in [2] is twice overestimated. As a result, in the limit of low pressures the rate constant (k_{-1}) [2] of the recombination reaction also appears overestimated [24] by factor of 15–30.

Now we shall calculate a preexponential factor for equilibrium (5) (Table 14, column 2), and then also values of equilibrium constant (5) (Table 14, column 3). Here the value of the rate constant $k_{5,\infty}$ of the direct reaction in the limit of high pressures is known [25, 26], therefore we find the values of the rate constant of recombination reaction (k_{-5}) by formula (2*) (Table 14, column 5). In a rather wide temperature range (from 1200 up to 1400 K) the rate constant $k_{-5,\infty}$ remains practically constant and equal to $10^{-10.6\pm0.1}$ cm^3 $molecule^{-1}$ s^{-1}, whereas the experimental value [26] for room temperature is $k_{-5,\infty}(300\ K) = 10^{-10.8\pm0.2}$ cm^3 $molecule^{-1}$ s^{-1}. Thus we obtain formula (13) for the whole investigated range.

$$k_{-5,\infty}(300\text{–}1400\ K)$$
$$= 10^{-10.8\pm0.2}(T/300\ K)^{0.3\pm0.1}\ cm^3\ molecule^{-1}\ s^{-1}. \quad (13)$$

Temperature dependence (13) agrees with the predictions of Gorin's model $T^{1/6}$ [22].

Further we shall calculate the preexponential factor for equilibrium (4) (Table 15, column 2) and then

Table 5. Thermodynamic functions of gas CF[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	146.471	29.101	2.906	175.548
200.00	166.634	29.184	5.818	195.732
298.15	178.261	29.841	8.708	207.480
300.00	178.440	29.858	8.764	207.664
400.00	186.883	31.034	11.806	216.413
500.00	193.518	32.234	14.973	223.467
600.00	199.018	33.251	18.247	229.438
700.00	203.739	34.046	21.615	234.626
800.00	207.892	34.661	25.052	239.216
900.00	211.604	35.138	28.541	243.325
1000.00	214.965	35.506	32.075	247.048
1100.00	218.037	35.795	35.640	250.446
1200.00	220.868	36.029	39.231	253.571
1300.00	223.496	36.213	42.844	256.462
1400.00	225.948	36.368	46.472	259.153
1500.00	228.245	36.494	50.116	61.667
1600.00	230.408	36.598	53.771	264.023
1700.00	232.450	36.686	57.436	266.245
1800.00	234.385	36.762	61.106	268.345
1900.00	236.225	36.824	64.787	270.332
2000.00	237.978	36.879	68.470	272.224
2500.00	245.681	37.067	86.964	280.474
3000.00	252.059	37.172	105.525	287.244
3500.00	257.504	37.234	124.126	292.980
4000.00	262.255	37.276	142.756	297.955
4500.00	266.469	37.305	161.402	302.348
5000.00	270.256	37.326	180.058	306.277
5500.00	273.694	37.343	198.724	309.838
6000.00	276.842	37.356	217.399	313.089

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

Table 6. Thermodynamic functions of gas CF_2[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	175.350	33.322	3.324	208.602
200.00	198.480	35.326	6.732	232.137
298.15	212.110	39.326	10.386	246.956
300.00	212.325	39.406	10.460	247.199
400.00	222.575	43.565	14.613	259.119
500.00	230.920	46.924	19.144	269.219
600.00	238.049	49.431	23.967	278.006
700.00	244.320	51.267	29.008	285.771
800.00	249.941	52.623	34.206	292.713
900.00	255.046	53.636	39.520	298.972
1000.00	259.726	54.405	44.923	304.662
1100.00	264.051	55.004	50.395	309.875
1200.00	268.071	55.472	55.921	314.683
1300.00	271.830	55.849	61.487	319.139
1400.00	275.358	56.154	67.087	323.289
1500.00	278.684	56.405	72.716	327.172
1600.00	281.828	56.610	78.366	330.821
1700.00	284.813	56.786	84.036	334.260
1800.00	287.649	56.933	89.723	337.507
1900.00	290.354	57.058	95.423	340.590
2000.00	292.939	57.167	101.133	343.519
2500.00	304.379	57.531	129.816	356.318
3000.00	313.935	57.736	158.637	366.828
3500.00	322.142	57.857	187.535	375.736
4000.00	329.333	57.937	216.485	383.468
4500.00	335.733	57.991	245.467	390.296
5000.00	341.499	58.033	274.472	396.409
5500.00	346.745	58.062	303.494	401.940
6000.00	351.557	58.083	332.531	406.994

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

values of equilibrium constant (4) (Table 15, column 3). Here the rate constant $k_{-4,\infty}(300\ \text{K}) = 10^{-10.2\pm0.2}$ cm^3 molecule^{-1} s^{-1} is known [27, 28] in the limit of high pressure, and therefore we find the values of the rate constant of dissociation reaction (4) by formula (2). Resulting rate constant (14) coincides within the limits of errors with our recommendation [29] for the range 600–1000 K. Therefore formula (14) can be recommended for the whole range 300–1000 K.

$$k_{4,\infty} = 10^{16.9\pm0.2} e^{-(541.7\pm2.0\ \text{kJ/mol})/RT}\ \text{s}^{-1}, \qquad (14)$$

$$300 \le T \le 1000\ \text{K}.$$

It is seen from the last column of Table 15 that the half-life of gaseous CF_4 at 1400 K is longer than 1000 s even if the back recombination reaction is neglected. Only at temperatures above 2000 K attained in shock waves the half-life of carbon tetrafluoride becomes less than a millisecond, which can be recorded by means of shock tubes [30].

Let us calculate a preexponential factor for equilibrium (3) (Table 16, column 2), and then values of the equilibrium (3) constant (Table 16, column 3). We estimate the values of the rate constants $k_{-3,\infty}(300\ \text{K}) = 10^{-10.3\pm0.2}$ cm^3 molecule^{-1} s^{-1} in the limit of high pressures by the interpolation of data for recombination reaction (k_{-1}) and (k_{-4}). We obtain the rate constant of dissociation (15) in the limit of high pressures (Table 16, column 5) by formula (2).

$$k_{3,\infty} = 10^{17.1\pm0.2} e^{-(521.4\pm4.0\ \text{kJ/mol})/RT}\ \text{s}^{-1}, \qquad (15)$$

$$300 \le T \le 1000\ \text{K}.$$

Table 7. Thermodynamic functions of gas CF_3[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	188.031	34.038	3.332	221.359
200.00	211.620	41.749	7.081	247.032
298.15	226.393	50.585	11.617	265.374
300.00	226.633	50.740	11.712	265.688
400.00	238.406	58.338	17.181	281.366
500.00	248.389	64.146	23.319	295.039
600.00	257.193	68.397	29.958	307.131
700.00	265.109	71.493	36.960	317.921
800.00	272.326	73.773	44.227	327.624
900.00	278.966	75.472	51.694	336.415
1000.00	285.116	76.769	59.308	344.439
1100.00	290.847	77.769	67.037	351.803
1200.00	296.213	78.560	74.855	358.606
1300.00	301.257	79.191	82.745	364.920
1400.00	306.017	79.702	90.689	370.807
1500.00	310.520	80.125	98.681	376.322
1600.00	314.795	80.472	106.712	381.505
1700.00	318.864	80.765	114.772	386.392
1800.00	322.743	81.012	122.861	391.016
1900.00	326.453	81.225	130.973	395.401
2000.00	330.005	81.405	139.104	399.572
2500.00	345.804	82.020	179.976	417.810
3000.00	359.089	82.359	221.077	432.797
3500.00	370.547	82.564	262.312	445.508
4000.00	380.620	82.702	303.628	456.546
4500.00	389.606	82.794	345.001	466.290
5000.00	397.717	82.861	386.414	475.018
5500.00	405.107	82.907	427.854	482.917
6000.00	411.895	82.945	469.317	490.135

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

Table 8. Thermodynamic functions of gas C_2F_5[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	224.288	52.004	4.143	265.722
200.00	256.383	75.166	10.517	308.972
298.15	279.394	94.325	18.869	342.695
300.00	279.789	94.647	19.045	343.280
400.00	299.420	109.814	29.302	372.686
500.00	316.702	121.111	40.877	398.472
600.00	332.271	129.337	53.419	421.316
700.00	346.470	135.316	66.667	441.730
800.00	359.545	139.721	80.429	460.098
900.00	365.893	143.018	94.575	470.993
1000.00	382.936	145.529	109.007	491.959
1100.00	393.488	147.479	123.662	505.925
1200.00	403.401	149.018	138.487	518.829
1300.00	412.743	150.248	153.452	530.803
1400.00	421.579	151.244	168.527	541.979
1500.00	429.956	152.064	183.694	552.439
1600.00	437.922	152.746	198.934	562.275
1700.00	445.510	153.319	214.238	571.555
1800.00	452.758	153.801	229.594	580.333
1900.00	459.692	154.215	244.997	588.660
2000.00	466.339	154.570	260.434	596.580
2500.00	495.970	155.771	338.049	631.215
3000.00	520.948	156.436	416.113	659.679
3500.00	542.532	156.838	494.436	683.825
4000.00	561.529	157.102	572.923	704.786
4500.00	578.492	157.286	651.519	723.301
5000.00	593.814	157.416	730.192	739.882
5500.00	607.783	157.512	808.923	754.890
6000.00	620.619	157.587	887.695	768.597

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

The comparison of the data of column 4 in Table 13 and of column 5 in Table 16 shows that in the range of 1000 1400 K the rate constant of dissociation (3) is less than the rate constant of dissociation (1) by 5–7 orders. That is why it was impossible to observe experimentally dissociation (3) when studying pyrolysis of hexafluoroethane in shock tubes [15, 31]. Rate constants $k_{3,\infty}$ and $k_{-3,\infty}$ are not measured so far.

We shall find equilibrium constant (6) from the data of Tables 6 and 11 (Table 17). The rate constant of recombination (k_{-6}) at room temperature was measured in the works [32, 33]. Hence for dissociation (6) we find rate constant (16) by formula (2).

$$K_{6,\infty} = 10^{14.6\pm0.1} e^{-(280\pm4\ \text{kJ/mol})/RT}\ \text{s}^{-1}, \quad 1000 \le T \le 1600\ \text{K}. \tag{16}$$

At last, we shall find equilibrium constant (7) from the data of Tables 6 and 9 (Table 18). For the recombination rate constant (k_{-7}) at room temperature we shall take a gas-kinetic limit of 10^{-10} cm^3 molecule^{-1} s^{-1}. Therefore, for dissociation (7) we obtain the rate constant (17) by formula (2).

$$k_{7,\infty} = 10^{18.2\pm0.1} e^{-(737\pm4\ \text{kJ/mol})/RT}\ \text{s}^{-1}, \quad 1000 \le T \le 1600\ \text{K}. \tag{17}$$

The comparison of the last columns of Tables 15 and 18 shows that the rate constant of dissociation for

Table 9. Thermodynamic functions of gas CF_4[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	179.052	35.096	3.353	212.589
200.00	203.258	48.686	7.485	240.693
298.15	219.313	62.652	12.969	262.822
300.00	219.580	62.886	13.088	263.211
400.00	232.998	73.995	19.958	282.901
500.00	244.756	82.162	27.787	300.340
600.00	255.333	88.041	36.312	315.867
700.00	264.993	92.279	45.341	329.775
800.00	273.885	95.384	54.729	342.310
900.00	282.128	97.697	64.391	353.686
1000.00	289.810	99.455	74.252	364.075
1100.00	297.000	100.814	84.267	373.619
1200.00	303.754	101.885	94.404	382.439
1300.00	310.124	102.743	104.635	390.631
1400.00	316.151	103.434	114.945	398.271
1500.00	321.865	104.003	125.318	405.425
1600.00	327.299	104.475	135.741	412.153
1700.00	332.478	104.873	146.209	418.500
1800.00	337.424	105.208	156.713	424.504
1900.00	342.157	105.492	167.248	430.199
2000.00	346.695	105.739	177.810	435.617
2500.00	366.930	106.567	230.907	459.311
3000.00	383.995	107.028	284.312	478.783
3500.00	398.743	107.304	337.899	495.306
4000.00	411.728	107.488	391.597	509.645
4500.00	423.322	107.613	445.373	522.314
5000.00	433.797	107.701	499.201	533.657
5500.00	443.347	107.768	553.067	543.924
6000.00	452.124	107.818	606.964	553.305

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

Table 10. Thermodynamic functions of gas CF_3I[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.000	212.054	42.079	3.542	247.479
200.000	238.964	59.430	8.661	282.282
298.150	257.679	71.903	15.135	308.457
300.000	257.989	72.104	15.269	308.901
400.000	273.554	81.459	22.972	331.000
500.000	286.977	88.124	31.471	349.933
600.000	298.876	92.810	40.531	366.443
700.000	309.587	96.132	49.988	381.012
800.000	319.341	98.534	59.728	394.016
900.000	328.298	100.308	69.673	405.727
1000.000	336.579	101.643	79.773	416.367
1100.000	344.281	102.672	89.991	426.107
1200.000	351.475	103.475	100.298	435.077
1300.000	358.230	104.120	110.679	443.383
1400.000	364.589	104.639	121.118	451.119
1500.000	370.601	105.061	131.603	458.353
1600.000	376.299	105.417	142.129	465.148
1700.000	381.715	105.710	152.683	471.545
1800.000	386.873	105.957	163.268	477.595
1900.000	391.799	106.170	173.872	483.331
2000.000	396.513	106.354	184.500	488.779
2500.000	417.429	106.969	237.843	512.586
3000.000	434.962	107.304	291.417	532.121
3500.000	450.052	107.513	345.125	548.677
4000.000	463.295	107.647	398.914	563.045
4500.000	475.095	107.739	452.758	575.731
5000.000	485.734	107.806	506.642	587.086
5500.000	495.420	107.852	560.557	597.362
6000.000	504.310	107.890	614.491	606.747

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

reaction (7) is less than that for the reaction (4) by 6–9 orders. Therefore reaction (7) is not observed on the background of fast reaction (4).

Thus the standard enthalpies of formation of some fluorinated molecules and radicals ($CF^{\cdot}$, $CF^{\cdot}_2$, $CF^{\cdot}_3$, CF_4, CF_3I, C_2F_4, $C_2F^{\cdot}_5$, and C_2F_6) calculated by a quantum mechanical method were used to find equilibrium and rate constants of dissociation of gaseous C_2F_6, C_2F_4, CF_4, and CF_3I. New enthalpies of formation of the molecules CF_3I, C_2F_6, and C_2F_4 noticeably differ from the values obtained earlier theoretically [6] or empirically [4, 5]. In particular, the new enthalpy of dissociation reaction (1) equal to 394.8±6.0 kJ mol^{-1} (Table 2) essentially differs from the value of 410.6±7.2 kJ mol^{-1} [2] obtained on the basis of the data [6]. As a result, the constant of equilibrium (1), which we have calculated, differs from the value, which was assumed as a basis of the work [2], by a factor of (15±5) at temperatures 700–1000 K and by a factor of (5±1) at 1300–1500 K (Table 13). The use of incorrect constant of equilibrium (1) leads to errors [2] in the calculation of the constant of recombination (1) from experimental data of the work [34] on dissociation (1).

This conclusion will not change in the case of possible future refinements of values of the reduced Gibbs energy for the radical $CF^{\cdot}_3$ (Table 7) or for the molecule C_2F_6 (Table 12). In fact, within the whole

Table 11. Thermodynamic functions of gas C_2F_4[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.000	197.483	44.230	3.641	233.915
200.000	225.456	65.033	9.129	271.111
298.150	245.404	80.413	16.309	300.114
300.000	245.746	80.656	16.456	300.612
400.000	262.645	91.990	25.117	325.448
500.000	277.400	100.501	34.760	346.933
600.000	290.597	106.944	45.146	365.853
700.000	302.570	111.843	56.097	382.727
800.000	313.555	115.601	67.478	397.915
900.000	323.703	118.509	79.187	411.706
1000.000	333.142	120.785	91.157	424.316
1100.000	341.963	122.592	103.328	435.914
1200.000	350.244	124.044	115.662	446.646
1300.000	358.046	125.224	128.127	456.625
1400.000	365.424	126.195	140.700	465.943
1500.000	372.418	126.998	153.360	474.675
1600.000	379.067	127.671	166.093	482.892
1700.000	385.404	128.241	178.890	490.653
1800.000	391.456	128.726	191.738	497.996
1900.000	397.246	129.140	204.632	504.967
2000.000	402.799	129.500	217.564	511.599
2500.000	427.563	130.730	282.651	540.644
3000.000	448.457	131.416	348.202	564.547
3500.000	466.524	131.839	414.020	584.835
4000.000	482.436	132.115	480.010	602.463
4500.000	496.652	132.303	546.115	618.035
5000.000	509.497	132.441	612.298	631.981
5500.000	521.213	132.542	678.545	644.608
6000.000	531.981	132.621	744.834	656.143

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

Table 12. Thermodynamic functions of gas C_2F_6[a]

T, K	Φ^0, kJ mol^{-1}	C^0_{eq}, J mol^{-1} K^{-1}	$H^0 - H^0_0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}
100.00	208.115	54.016	4.185	249.956
200.00	241.182	83.530	11.090	296.633
298.15	265.824	106.936	20.483	334.544
300.00	266.251	107.325	20.683	335.205
400.00	287.764	125.533	32.369	368.698
500.00	306.962	139.035	45.632	398.241
600.00	324.403	148.843	60.051	424.504
700.00	340.409	155.972	75.310	448.014
800.00	355.203	161.215	91.183	469.198
900.00	368.953	165.139	107.508	488.428
1000.00	381.791	168.131	124.176	505.988
1100.00	393.822	170.449	141.110	522.126
1200.00	405.141	172.277	158.249	537.037
1300.00	415.825	173.737	175.553	550.886
1400.00	425.937	174.926	192.985	563.807
1500.00	435.535	175.900	210.528	575.911
1600.00	444.666	176.708	228.160	587.287
1700.00	453.373	177.386	245.863	598.023
1800.00	461.693	177.963	263.632	608.178
1900.00	469.656	178.453	281.453	617.814
2000.00	477.294	178.875	299.319	626.977
2500.00	511.377	180.302	389.147	667.063
3000.00	540.148	181.089	479.511	700.012
3500.00	565.029	181.570	570.179	727.966
4000.00	586.942	181.884	661.044	752.233
4500.00	606.519	182.101	752.041	773.668
5000.00	624.207	182.256	843.126	792.864
5500.00	640.339	182.369	934.280	810.240
6000.00	655.166	182.457	1025.484	826.110

[a] Calculated from data of Tables 3, 4 and the last column of Table 1.

range of 700–1500 K the values of preexponential factor (8) for i = 1, which we have calculated from Tables 7 and 12, differ only in the third figure after comma from the results calculated by means of Tables [4, 5]. Meanwhile, the authors of [4, 5] calculated thermodynamic functions of C_2F_6 in view of the hindered internal rotation and nonlinearity of molecular large-amplitude vibrations. The data of Tables 8 and 12 were found using the program Gaussian-3, in which all the molecular modes are treated simplistically as harmonic vibrations [35]. However, in spite of it, the calculated values of preexponential factor (8) for i = 1 have changed no more than by 1–2% over the last 30 years. The principal difference between equilibrium constants $K_{c,1}$, which we presented in Table 13, and those obtained by the authors of [2] results from the adoption of a new value of $\Delta_{r,1}H^0_0$ (Table 2).

Our new values of the enthalpy of formation for $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, and C_2F_6 appeared higher (by 6, 13, 15 kJ mol^{-1}, respectively) than the values published earlier [4, 5]. Because of this symbasis the enthalpies of reactions $\Delta_{r,i}H^0_T$, which we have calculated for i = 1 and 3, are very close to those, which were found earlier [1, 3] from tables the [4, 5] (Table 2). On the contrary, the authors of [2] used the new value [6] of the enthalpy of the radical $CF_3^{\cdot}$ formation, but have not dared to deviate from tables [4, 5] with respect to the enthalpy of the molecule C_2F_6 formation. It was the reason which has led to the unreal high value of

Table 13. Calculuation of the rate constant of the back recombination reaction (k_{-1}) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,1}/R$)/n cm^{-3}] (Tables 7, 12)	log ($K_{c,1}$/cm^{-3}) (this work)	log ($k_{1,\infty}$/s^{-1}) [formula (11)]	log ($k_{-1,\infty}$/cm^3 s^{-1}) (this work)	log ($K_{c,1}$/cm^{-3}) [2]	log($k_{-1,\infty}$/cm^3 s^{-1}) [2]
298.15	29.15696±0.026[a]	–39.98±0.74[b]				
300	29.15703±0.026	–39.55±0.74				
700	28.935±0.001	–0.51±0.31		–10.80±0.05[c]	–1.72	–10.6
1000	28.709±0.008	8.09±0.22			7.23	
1200	28.569±0.010	11.39±0.19				
1300	28.503±0.009	12.65±0.17	2.0±0.2	–10.7±0.37	11.96	–10.4
1400	28.440±0.008	13.72±0.16	3.1±0.2	–10.6±0.36		
1500	28.379±0.007	14.64±0.15	4.1±0.2	–10.5±0.35	14.04	

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2). [c] Data of [1]. Hereafter n is a number of particles.

Table 14. Calculuation of the rate constant of the back recombination reaction (k_{-5}) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,5}/R$)/n cm^{-3}] (Tables 7, 10)	log ($K_{c,5}$/cm^{-3}) (this work)	log ($k_{5,\infty}$/s^{-1}) [25, 26]	log ($k_{-5,\infty}$/cm^3 s^{-1}) (this work)
298.15	26.10917±0.0048[a]	–13.53±0.72[b]		
300	26.10944±0.0048	–13.29±0.72		
700	25.977±0.009	9.09±0.31		
1000	25.844±0.010	14.02±0.22		
1200	25.764±0.011	15.91±0.18	5.3±0.2	–10.61±0.38
1300	25.727±0.011	16.63±0.17	6.1	–10.53±0.37
1400	25.692±0.012	17.25±0.15	6.7	–10.55±0.35

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2).

Table 15. Calculuation of the thermal dissociation rate constant (k_4) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,4}/R$)/n cm^{-3}] (Tables 7, 10)	log ($K_{c,4}$/cm^{-3}) (this work)	log ($k_{-4,\infty}$/cm^3 s^{-1}) [27, 28]	log ($k_{4,\infty}$/s^{-1}) (this work)
298.15	26.905±0.010[a]	–67.88±0.36[b]		
300	26.908±0.010	–67.29±0.36	–10.2±0.1	–77.5±0.6
400	27.028±0.002	–43.62±0.27	–10.2±0.1	–53.8±0.5
700	27.153±0.027	–13.22±0.18	–10.2±0.1	–23.4±0.4
1000	27.156±0.035	–1.10±0.14		–11.3±0.3
1200	27.173±0.038	3.62±0.12		–6.6±0.3
1400	27.108±0.041	6.92±0.11		–3.3±0.3
2000	27.012±0.046	12.88±0.10		+2.7±0.3

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2).

$\Delta_{r,1}H^0_{298}$ = 413.2 kJ mol^{-1} [2] (Table 2). The authors of [6] also have not dared to deviate from the tables [4, 5] in this point. Meanwhile, the results obtained in the present work (Table 1, 2, and 13) give serious grounds to revise the value of $\Delta_f H^0_{298}(C_2F_6)$ = –1344 kJ mol^{-1} recommended in the tables [4, 5]. By the way, the direct experimental measuring of the enthalpy of hexafluoroethane formation fulfilled 55 years ago [36] has given the value of $\Delta_f H^0_{298}(C_2F_6)$ = –1310 kJ mol^{-1}, which is much closer to our value of –1328.9 kJ mol^{-1}

Table 16. Calculuation of the thermal dissociation rate constant (k_3) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,3}/R$)/n cm^{-3}] (Tables 8, 12)	log ($K_{c,3}$/cm^{-3}) (this work)	log ($k_{-3,\infty}$/cm^3 s^{-1})	log ($k_{3,\infty}$/s^{-1}) (this work)
298.15	27.244±0.41[a]	–64.88±1.12[b]		
300	27.247±0.41	–64.32±1.12	–10.3±0.2	
400	27.35±0.42	–41.32±0.90	–10.3±0.2	
700	27.46±0.43	–11.78±0.73	–10.3±0.2	
1000	27.46±0.44	–0.01±0.65		–10.3±0.9
1200	27.44±0.43	4.55±0.60		–5.8±0.8
1400	27.41±0.43	7.79±0.53		–2.5±0.7

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2).

Table 17. Calculuation of the the thermal dissociation rate constant (k_6) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,6}/R$)/n cm^{-3}] (Tables 6, 11)	log ($K_{c,6}$/cm^{-3}) (this work)	log ($k_{-6,\infty}$/cm^3 s^{-1}) [32, 33]	log ($k_{6,\infty}$/s^{-1}) (this work)
300	28.096±0.009[a]	–20.64±0.70[b]	–13.2±0.1	
700	28.082±0.008	7.20±0.31		
1000	27.928±0.008	13.31±0.21		–0.7±0.21
1200	27.822±0.008	15.64±0.18		1.8±0.18
1400	27.719±0.008	17.28±0.16		3.5±0.16
1600	27.621±0.008	18.48±0.13		5.3±0.13

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2).

Table 18. Calculuation of the thermal dissociation rate constant (k_7) in the limit of high pressures

T, K	log [exp($\Delta\Phi^0_{c,7}/R$)/n cm^{-3}] (Tables 6, 9)	log ($K_{c,7}$/cm^{-3}) (this work)	log ($k_{-7,\infty}$/cm^3 s^{-1})	log ($k_{7,\infty}$/s^{-1}) [formula (17)]
300	28.060±0.283[a]		–10.0±0.1	
1000	28.315±0.232	–10.18±0.43[b]		–20.2±0.2
1200	28.265±0.225	–3.81±0.40		–13.8
1400	28.208±0.220	0.71±0.38		–9.3
1600	28.149±0.216	4.09±0.35		–5.9
1800	28.090±0.212	6.71±0.33		–3.3

[a] The errors show a difference between calculations on the basis of Tables 5–12 and Tables [4, 5]. [b] The error includes the error of the previous column plus the error in the reaction heat in the exponential term of formula (2).

than to the recommendations of [4–7]. We hope that the results presented here will stimulate not only theoretical, but also experimental new researches in the field of the thermochemistry of fluorocarbons.

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