Statistical Thermodynamics

Enthalpy, Free Energy, Entropy, and Heat Capacity of Some Hexafluorides of Octahedral Symmetry *

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A detailed analysis of the molecular structural data and infrared absorption and Raman spectra of the hexafluoride of sulfur, selenium, tellurium, molybdenum, technetium, ruthium, rhodium, tungsten, thenium, osmium, iridium, platinum, uranium, neptunium, and plutonium has been made. These molecules, having the greatest number of symmetry elements of all existing molecules, possess an octahedral symmetry with the symmetry point group O_h. They give rise to six fundamental frequencies of which three are allowed in the Raman spectrum, two are allowed in the infrared absorption spectrum, and one is inactive. The inactive mode in normally determined from the overtones and combinations. On the basis of a rigid rotator and harmonic oscillator model, enthalpy, free energy, entropy, and heat capacity for temperatures from 200 °K to 2000 °K have been computed for these molecules. The results are briefly discussed and compared with available experimental data.

Introduction

From the results of electron diffraction studies, EWING and SUTTON [1] suggested an octahedral symmetry for sulfur and selenium hexafluoride, SEIP and SKOLEVIK [2] for tellurium hexafluoride, and SEIP and SEIP [3] for molybdenum and tungsten hexafluoride. The earlier data for sulfur hexafluoride are from BROCKWAY and PAULING [4]. The structure of the hexafluorides of molybdenum, tungsten, and uranium was studied by BRAUNE and PINNOW [5]. The most consistent model was an octahedron in which the X-F distances lay along the rectangular axes, and were in the ratio 1.00 to 1.12 to 1.22 for all three compounds. They did not, however, entirely exclude the regular octahedron in which all the X-F distances are equal. However, tungsten hexafluoride belongs to the point group O_h [6,7]. BAUER [8] studied uranium hexafluoride and found that, while his experimental results were to some extent in harmony with those of BRAUNE and PINNOW [5], a more careful interpretation appeared to rule out the structure proposed by them, as well as the totally symmetric one. He proposed, instead, a model without a center of symmetry as the one which best fit his data. But, even then, he himself pointed out two major difficulties with this model. Recently, SEIP [9] confirmed an octahedral symmetry for uranium hexafluoride. SCHOMAKER, KIMURA and WEINSTOCK [10] determined internuclear distances and confirmed an octahedral symmetry for two hexafluorides of tungsten, osmium, iridium, uranium, neptunium, and plutonium. A brief survey of two structural data was recently reported by SEIP [11] for the hexafluorides of tellurium, molybdenum, tungsten, and uranium. Although the structure for the hexafluorides of technetium, ruthenium, and rhodium is well known from their vibrational assign-

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ments, the internuclear distances were not determined experimentally. Recently, the Te-F, Ru-F, and Rh-F distances were evaluated as 1.8512 Å, 1.8775 Å, and 1.8738 Å, respectively, from the stretching force constants of these molecules and from the Badger's empirical relation[12] by NAGARAJAN[13,14]. From high resolution infrared spectra and other molecular structural studies, several investigators[15–20] reported internuclear distances for the hexafluorides of rhenium, osmium, iridium, platinum, uranium, neptunium, and plutonium.

The Raman and infrared absorption spectra of the group VIA hexafluorides of sulfur, selenium, and tellurium were first completely investigated by GAUNT[21,22]. The normal modes of six oscillations (three valency vibrations and three deformation vibrations) for an octahedral molecule of this type have been given[23–25]. One fundamental frequency for selenium hexafluoride and three fundamental frequencies for sulfur and tellurium hexafluoride were assigned to the gaseous state from Raman spectra[26,27]. Recently, CLAASSEN, GOODMAN, HOLLOWAY, and SELIG[28] studied the Raman spectra of these group VIA hexafluorides in the gaseous state by using powerful laser sources and correctly reassigned the fundamentals. The new values of the fundamentals in cm^{-1} are given in Table 1. The Raman and infrared absorption spectra of the group VIB hexafluorides of molybdenum and tungsten were studied by many investigators. The Raman spectra of molybdenum hexafluoride have been studied in both liquid[19,29] and gaseous[30] states but with poor resolution and without overtones. The infrared absorption and Raman spectra of this compound and tungsten hexafluoride were studied by GAUNT[21]. Recently, CLAASSEN and his co-workers[28,31] studied the Raman spectra of these compounds in the gaseous state and accurately reassigned the fundamentals. The recent values of the fundamentals for the hexafluorides of molybdenum and tungsten are given in Table 1.

Recently, WEINSTOCK and GOODMAN[32] presented a detailed review of electronic, infrared absorption, and Raman spectra of all the then existing hexafluorides. The hexafluorides of rhenium, technetium, and osmium were of particular interest because they offered an almost unique opportunity to study the spectra of molecules with vibronic coupling associated with the dynamic Jahn-Teller effect which was used to account for the unusual widths of certain vibrational bands observed by WEINSTOCK and CLAASSEN[33]. Although marked broadening of some of the bands was observed, the vibronic subbands[32] were not identifiable in the Raman spectra of rhenium and osmium hexafluoride[31]. The infrared spectrum in the gaseous state and Raman spectrum in the liquid state were studied for technetium hexafluoride by CLAASSEN, SELIG, and MALM[30] who found that technetium hexafluoride exhibited vibronic coupling to an even greater extent than the hexafluorides of rhenium and osmium. The Raman and infrared absorption spectra of rhenium hexafluoride were studied by GAUNT[34]. CLAASSEN and his associateds[28] studied the Raman spectra of the group VIIB hexafluorides of technetium and rhenium in the gaseous state with powerful laser sour-

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Table 1. Fundamental frequencies in cm^{-1} for fifteen hexafluorides of octahedral symmetry.

Molecule	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$
Sulfur Hexafluoride	773.5	641.7	939	614	525	347
Selenium Hexafluoride	706.9	658.7	780	437	405	264
Tellurium Hexafluoride	697.1	670.3	752	325	314	197
Molybdenum Hexafluoride	741.5	651.6	741.1	264	318	116
Technetium Hexafluoride	712.9	639	748	265	297	145
Ruthenium Hexafluoride	675	624	735	275	283	186
Rhodium Hexafluoride	634	595	724	283	269	192
Tungsten Hexafluoride	771	677.2	711	258	320	127
Rhenium Hexafluoride	753.7	671	715	257	295	147
Osmium Hexafluoride	730.7	668	720	268	276	205
Iridium Hexafluoride	701.7	645	719	276	267	206
Platinum Hexafluoride	656.4	601	705	273	242	211
Uranium Hexafluoride	667.1	532.5	624	186.2	202	142
Neptunium Hexafluoride	654	535	624	198.6	208	164
Plutonium Hexafluoride	628	523	616	206	211	173

ces, observed the Jahn-Teller effect with over-all frequency differences from 6 to 16 cm^{-1}, and correctly assigned the fundamentals, and many overtones and combinations. The new values of their fundamental frequencies are given in Table 1.

The Raman and infrared absorption spectra of ruthenium and rhodium hexafluoride were first studied in both liquid and gaseous states by WEINSTOCK, CLAASSEN and CHERNICK[35] and all the fundamentals except the inactive mode were assigned. The values of the inactive mode for these two hexafluorides were evaluated from the normal coordinate analysis by NAGARAJAN[36]. Then the values of all the fundamentals were reassigned by WEINSTOCK and GOODMAN[32] and they are given in Table 1. The Raman and infrared absorption spectra in both the liquid and gaseous states have been studied for osmium[16], platinum[16], and iridium[17] hexafiuoride. These three hexafluorides were reinvestigated in the vapor along with other hexafluorides, their spectra were analyzed, and their fundamentals given in Table 1, were correctly reassigned by CLAASSEN and SELIG[31]. The Raman spectra of uranium hexafluoride were studied in both liquid[37] gaseous states[18] and their assignments were in good agreement with each other. The Raman and infrared absorption spectra of uranium hexafluoride were studied in both liquid and gaseous states[19, 21, 38] and its fundamentals, given in Table 1, were assigned. CLAASSEN and his associates[28] reinvestigated the Raman spectrum of uranium hexafluoride along with other hexafluorides in the gaseous state but their assignments of the fundamentals were similar to those of the previous ones. The Raman and infrared absorption spectra of neptunium and plutonium hexafluoride were studied in both liquid and gaseous states by MALM, WEINSTOCK and CLAASSEN[20] and the fundamentals were assigned. Later, the same studies were undertaken for neptunium hexafluoride by GASNER and FRLEC[39] and the fundamentals were reassigned. Recently, WEINSTOCK and GOODMAN[32] reinvestigated these two hexafluorides along with other hexafluorides and correctly reassigned the fundamentals as they are given in Table 1. On the basis of these recent vibrational and structural data, it is aimed here to compute the four thermodynamic quantities, namely, enthalpy, free energy, entropy, and heat capacity on the assumption of a rigid rotator and harmonic oscillator model. The results of the present investigation should be very useful for the evaluation of normal frequencies in other related fluorine-containing compounds, and for the interpretation of the results of experimental thermodynamic quantities, particularly, the entropies and heat capacities at normal pressures.

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Thermodynamic Functions

One of the best applications of the study of infrared absorption and Raman spectra of polyatomic molecules and other molecular structural determinations is that thermodynamic functions can be statistically computed, namely, enthalpy function $(H_0 - H_0{}^0)/T$, free enthalpy or Gibbs free energy function $(F_0 - H_0^0)/T$, entropy S^0, and heat capacity C_p^0. A rigid rotator and harmonic oscillator model is assumed for each molecule, and all four thermodynamic quantities are computed for a gas in the thermodynamic standard gaseous state of unit fugacity (one atmosphere) for the temperature range from 200°K to 2000°K. The vibrational, translational, and rotional contributions to the total thermodynamic quantities would be computed in the following manner:

The contribution due to molecular vibrations is obtained by summing the appropriate harmonic oscillator function G_{ho} from standard tables of functions[40] over all the normal modes of oscillation of the molecule. For the doubly or triply degenerate vibrations, the term must be doubled or tripled as appropriate. Thus, the vibrational contributions will be given as

$$G_{\text{v}} = \sum_i G_{\text{ho}}\, u_i$$

where d_i is the degeneracy, G_{ho} is the harmonic oscillator function, u_i is the internal thermal energy, and the sum covers all the normal modes. The internal thermal energy, $u_i = h c w_i/T$, is calculated for each normal mode, where h is the Planck's constant, c is the velocity of light, w_i is the ith normal mode in cm^{-1}, and T is the absolute temperature. For each normal mode, the harmonic oscillator contributions to the four thermodynamic quantities, namely, C/R, $(H - H_0)/R\,T$, $-(F - H_0)/R\,T$, and S/R, are entered in a tabular form from the standard tables of thermodynamic functions[40] for the corresponding values of the internal thermal energies. After summing up all these values under each column, each total is multiplied by the gas constant R in order to obtain the quantities C, $(H - H_0)/T$, $-(F - H_0)/T$, and S. The value under the column of heat capacity, C, is added with $4\,R$ in order to get the value of heat capacity at constant pressure, C_p^0, for the harmonic oscillator approximation at a pressure of one atmosphere. Similarly, the value under the column of enthalpy function, $(H - H_0)/T$ is added with $4\,R$ in order to get the value of enthalpy function, $(H_0 - H_0^0)/T$, for the harmonic oscillator approximation at one atmosphere. The value under column S represents the vibrational contribution to the free energy function.

[40] K. S. Pitzer, Quantum Chemistry, Prentice-Hall, Inc., New York 1953.

From the molecular structural data, the rotational and translational contributions to the entropy, heat capacity, and free energy function for one mole of a perfect gas at one atmosphere were obtained from the following relations:

$$S_{\text{tr}}^0 + S_{\text{r}}^0 = 2.2868\,(8 \log T + 3 \log M + \log I_{xx}\, I_{yy}\, I_{zz} - 2 \log \sigma) - 7.6965,$$

$$-(F_{\text{tr}}^0 + F_{\text{r}}^0 - H_0^0)/T = S_{\text{rt}}^0 + S_{\text{r}}^0 - 4\,R\,,$$

$$(C_p^0)_{\text{tr}} + (C_p^0)_{\text{r}} = (H_{\text{tr}}^0 + H_{\text{r}}^0 - H_0^0)/T = 4\,R\,.$$

Here S, F, C_p, H, tr, r, T, M, and σ stand for entropy, free energy, heat capacity at constant pressure, enthalpy, translational part, rotational part, temperature in degrees Kelvin, total mass of the molecule, and symmetry number of the point group to which the molecule belongs, respectively, and I_{xx}, I_{yy}, and I_{zz} are the principal moments of inertia in atomic mass units times Å^2 along the x-axis, y-axis, and z-axis, respectively. The value of the gas constant, R, is 1.9872 cal/deg mole. These contributions due to translation and rotation are added to the contribution due to vibration in order to obtain the total contribution to the free energy function $-(F_0 - H_0^0)/T$, and the entropy, S^0.

Results

The hexafluorides of sulfur, selenium, tellurium, molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium, platinum, uranium, neptunium, and plutonium have 10 different symmetry elements and 48 different symmetry operations, the highest possible number of symmetry operations ever found in a molecule. These molecules, as described earlier, possess an octahedral symmetry with the symmetry point group O_h. Each molecule possessing several planes of symmetry gives rise, according to the relevant symmetry properties and selection rules[24], to 15 vibrational degrees of freedom which, in turn, constitute only 6 genuine normal (fundamental) modes. The 21 Cartesian displacement vectors generate the representation τ in the following manner:

$$\tau = \text{A}_{1\text{g}} + \text{E}_\text{g} + \text{F}_{1\text{g}} + 3\,\text{F}_{1\text{u}} + \text{F}_{2\text{g}} + \text{F}_{2\text{u}}\,.$$

According to the symmetry operations and selections rules (see [24]), the rotations and translations belong, respectively, to the F_{1g} and F_{1u} representations. After deleting these, we obtain the following list of genuine normal modes, grouped according to the activities of their fundamentals:

$$\tau_v = A_{1g}(R; p) + E(R; dp) + 2\,F_{1u}(I; \|) + F_{2g}(R; dp) + F_{2u}(\text{inactive})$$

where R, I, p, dp, and $\|$ stand for Raman active, infrared active, polarized, depolarized, and parallel, prespectively. The gerade modes are only Raman active, while the ungerade ones are only infrared active. None of the bands observed in the Raman spectrum is observed in the infrared absorption spectrum, thereby indicating that Pauli's exclusion principle is obeyed here, as it must be, since the molecule has a center of symmetry. Further, the occurrence of a genuine normal vibration which is completely inactive as a fundamental must be noted. This is a rare phenomenon in the field of molecular spectroscopy but is occasionally encountered in relatively highly symmetrical molecules. The fundamental frequencies in cm^{-1} for all the 15 hexafluorides are given in Table 1. On the basis of electron diffraction, microwave, and other structural studies described earlier for all these 15 hexafluorides, the following values of the interatomic distances were adopted for the computations of the principal moments of inertia: S-F = 1.58 Å, Se-F = 1.70 Å, Te-F = 1.84 Å, Mo-F = 1.83 Å, Te-F = 1.8512 Å, Ru-F = 1.8775 Å, Rh-F = = 1.8738 Å, W-F = 1.83 Å, Re-F = 1.92 Å, Os-F = 1.831 Å, Ir-F = 1.833 Å, Pt-F = 1.829 Å, U-F = 1.994 Å, Np-F = 1.98 Å, and Pu-F = 1.972 Å. The computed values of the principal moments of inertia $I_{xx} = I_{yy} = I_{zz}$ in units AWU Å^2 and gcm^2 are as follows:

Interatomic distances	$I_{xx} = I_{yy} = I_{zz}$ AWA Å^2	10^{40} g cm^2
$S\text{-}F_6$	189.7264	315.1602
$Se\text{-}F_6$	219.6400	364.8506
$Tl\text{-}F_6$	257.3056	427.4181
$Mo\text{-}F_6$	254.5164	422.7848
$Te\text{-}F_6$	260.4475	432.6372
$Ru\text{-}F_6$	267.9005	445.0176
$Rh\text{-}F_6$	266.8456	443.2652
$W\text{-}F_6$	254.5164	422.7848
$Re\text{-}F_6$	280.1664	465.3928
$Os\text{-}F_6$	254.7946	423.2469
$Ir\text{-}F_6$	255.3516	424.1722
$Pt\text{-}F_6$	254.2383	422.3229
$U\text{-}F_6$	302.1787	501.9581
$Np\text{-}F_6$	297.9504	494.9343
$Pu\text{-}F_6$	295,5476	490.9429

Assumed in the computations were a symmetry number of 24, a singlet ground electronic state, and chemical atomic weights[41]. Neglected in the calculations were the contributions due to the centrifugal distortion, isotopic mixing, nuclear spins, and interaction between vibration and rotation, since the contributions of these are negligibly small compared to the total thermodynamic quantities due to vibration, rotation, and translation. The computed values of all four thermodynamic quantities in calories per degree mole are given in Table 2 for the 15 hexafluorides.

It is seen from the results for these hexafluorides that the values of heat capacity increase rapidly from 200° to 1000 °K, and beyond 2000 °K the increase with temperature is negligibly small. Similarly, the values of entropy increase rapidly from 200° to 1500 °K, and beyond 1500 °K they increase slowly but uniformly. While the values of the enthalpy and free enthalpy functions increase very rapidly near and a little above room temperature, they increase slowly but uniform at higher temperatures. The values of all four thermodynamic quantities at every temperature are, as expected, in increasing order from sulfur to selenium hexafluoride and from selenium to tellurium hexafluoride. This clearly shows that the replacement of a central atom with an atom of higher atomic weight causes lower fundamental frequencies, and correspondingly higher thermodynamic quantities. This is true for the compounds of A-group elements of the periodic table. But, this situation is not observed for many compounds of B-group elements. As an example, all four thermodynamic quantities at a particular temperature for tungsten hexafluoride are not greater than those of molybdenum hexafluoride. Some are greater and some are more or less similar. The reason is that all the observed fundamental frequencies of tungsten hexafluoride are not smaller than those of molybdenum hexafluoride. Actually, some are smaller, some are greater, some are in the same range, and finally all of them are in an irregular order (see Table 1). The same observation may be made for the group VIIB hexafluorides, namely, those of technetium and rhenium, and for the group VIII hexafluorides, namely, those of ruthenium and osmium, and rhodium and iridium. Similarly, the

[41] R. C. WEAST, Handbook of Chemistry and Physics, 49th edition, The Chemical Rubber Company, Cleveland, Ohio 1968—1969.

Table 2. Enthalpy, free energy, entropy, and heat capacity of fifteen hexafluorides for the ideal gaseous state at a pressure of one atmosphere. (All the quantities are in cal/deg mole.)

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
		Sulfur hexafluoride		
200	10.2817	51.3673	61.6490	15.9623
273.16	12.7358	54.9754	67.7112	21.6697
298.16	13.5692	56.1389	69.7081	23.2495
300	13.6235	56.2198	69.8433	23.2856
400	16.6286	60.5475	77.1761	27.7917
500	19.1904	64.5748	83.7652	30.6543
600	21.2643	68.2512	89.5155	32.4932
700	22.9611	71.6640	94.6251	33.7129
800	24.3842	74.8676	99.2518	34.5713
900	25.5306	77.7717	103.3023	35.1689
1000	26.5145	80.4810	106.9955	35.6200
1100	27.3612	83.0816	110.4428	35.9569
1200	28.0721	85.4054	113.4775	36.2207
1300	28.7254	87.7866	116.5120	36.4276
1400	29.2801	89.8659	119.1460	36.6356
1500	29.7929	92.0221	121.8150	36.8437
1600	30.2232	93.9244	124.1476	36.8466
1700	30.6386	95.8579	126.4965	36.9439
1800	30.9520	97.4321	128.3841	37.0145
1900	31.2804	99.1888	130.4692	37.0831
2000	31.4368	100.2741	131.7109	37.1118
		Selenium hexafluoride		
200	12.1359	53.5166	65.6525	20.0569
273.16	14.9742	57.7284	72.7026	25.0829
298.16	15.8800	59.0843	74.9643	26.4118
300	15.9239	59.1589	75.0828	26.4841
400	19.0931	64.2017	83.2948	30.2834
500	21.5880	68.7542	90.3386	32.5768
600	23.5410	72.8732	96.4144	33.9754
700	25.1181	76.6435	101.7616	34.9025
800	26.3746	80.0754	106.4500	35.5245
900	27.4024	83.2066	110.6090	35.9607
1000	28.2829	86.1519	114.4348	36.2891
1100	29.0428	88.9738	118.0166	36.5387
1200	29.6567	91.4383	121.0950	36.7215
1300	30.2216	93.8938	124.1154	36.8758
1400	30.6727	96.0409	126.7136	36.9876
1500	31.1081	98.2457	129.3538	37.0724
1600	31.4994	100.2781	131.7775	37.1695
1700	31.8316	102.2543	134.0859	37.2331
1800	32.1405	104.0705	136.2110	37.2903
1900	32.3853	105.6650	138.0503	37.3334
2000	32.6671	107.5124	140.1795	37.3785
		Tellurium hexafluoride		
200	14.2678	56.0095	70.2773	22.6971
273.16	16.9771	60.8465	77.8256	26.9823
298.16	17.8712	62.3674	80.2385	28.1007
300	17.9441	62.4948	80.4389	28.2404
400	20.9390	68.0670	89.0060	31.4197
500	23.2364	72.9803	96.2167	33.3387
600	25.0475	77.4493	102.4968	34.5398
700	26.4402	81.3873	107.8275	35.3067
800	27.6406	85.1389	112.7795	35.8627
900	28.5528	88.3917	116.9445	36.3209
1000	29.3365	91.4208	120.7573	36.5105
1100	29.9679	94.0819	124.0498	36.7132
1200	30.5338	96.6807	127.2145	36.8740
1300	31.0366	99.2000	130.2366	370027.
1400	31.4962	101.7554	133.2516	37.1059
1500	31.8595	103.8044	135.6639	37.1872
1600	32.1812	105.8134	137.9946	37.2509
1700	32.4367	107.4771	139.9138	37.3036
1800	32.7412	109.5656	142.3068	37.3547
1900	32.9705	111.2506	144.2211	37.3934
2000	33.2286	113.2206	146.4492	37.4324
		Molybdenum hexafluoride		
200	15.6811	57.6675	73.3486	23.8685
273.16	18.4280	62.9703	81.3983	27.7305
298.16	19.2519	64.6169	83.8688	28.7561
300	19.2920	64.6923	83.9843	28.8266
400	22.0892	70.6540	92.7432	31.8201
500	24.8835	75.8835	100.1141	33.6082
600	25.8917	80.4082	106.2999	34.7228
700	27.2209	84.5183	111.7392	35.4629
800	28.2903	88.2446	116.3490	35.9660
900	29.1744	91.7773	120.9517	36.3217
1000	29.8333	94.5268	124.3601	36.5620
1100	30.5034	97.6731	128.1765	36.7728
1200	31.0123	100.1727	131.1850	36.9219
1300	31.4902	102.7536	134.2438	37.0449
1400	31.8801	105.0491	136.9292	37.1399
1500	32.2732	107.5590	139.8312	37.2215
1600	32.5414	109.5119	142.0533	37.2782
1700	32.8247	111.3286	144.1533	37.3334
1800	33.1114	113.5794	146.6908	37.3819
1900	33.3129	114.9753	148.2882	37.4185
2000	33.5281	117.0143	150.5424	37.4509
		Technetium hexafluoride		
200	15.4084	57.4430	72.8514	23.9299
273.16	18.2582	62.6990	80.9573	27.8255
298.16	19.0985	64.3153	83.4138	28.9113
300	19.1525	64.4144	83.5669	28.9200
400	21.9954	70.3554	92.3508	31.8845
500	24.1791	75.5067	99.6858	33.6670
600	25.8450	80.0199	105.8649	34.7705
700	27.1878	84.1632	111.3510	35.4935
800	28.2620	87.8816	116.1436	35.9913
900	29.1497	91.3536	120.5033	36.3362
1000	29.8526	94.2846	124.1372	36.5894
1100	30.4631	97.1232	127.5863	36.7822
1200	31.0018	99.9060	130.9078	36.9326
1300	31.4741	102.4424	133.9165	37.0520
1400	31.8901	104.8210	136.7111	37.1490
1500	32.2555	107.0994	139.3549	37.2279
1600	32.5492	109.0070	141.5562	37.2909
1700	32.8616	111.3144	144.1760	37.3447
1800	33.0613	112.6910	145.7523	37.3823
1900	33.3185	114.8252	148.1437	37.4226
2000	33.5349	116.7560	150.2909	37.4552

Ruthenium hexofluoride

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	14.9240	56.4190	71.3430	23.8264
273.16	17.8946	61.5330	79.4276	27.8727
298.16	18.7771	63.1353	81.9124	28.9264
300	18.8391	63.2563	82.0954	28.9963
400	21.7871	69.0883	90.8754	31.9966
500	23.9888	74.2315	98.2203	33.7249
600	25.7498	78.8031	104.5529	34.8436
700	27.1212	82.9127	110.0339	35.5578
800	28.2139	86.6303	114.8442	36.0429
900	29.0806	89.8712	118.9518	36.3805
1000	29.8148	92.9033	122.7181	36.6329
1100	30.4555	95.9321	126.3876	36.8177
1200	30.9897	98.5937	129.5834	36.9626
1300	31.4646	101.0683	132.5329	37.0792
1400	31.8615	103.4661	135.3276	37.1667
1500	32.2281	105.6635	137.8916	37.2456
1600	32.5259	107.6330	140.1589	37.3034
1700	32.8113	109.6308	142.4421	37.3547
1800	33.0405	111.3765	144.4170	37.3930
1900	33.2990	113.4290	146.7280	37.4322
2000	33.5061	115.2168	148.7229	37.4627

Rhodium hexafluoride

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	14.9786	56.4062	71.3848	24.0871
273.16	18.0025	61.5469	79.5494	26.3710
298.16	18.8761	63.1351	82.0112	29.1857
300	18.9645	63.2767	82.2412	29.2771
400	21.9394	69.1527	91.0921	32.2170
500	24.2159	74.3784	98.5943	33.9405
600	25.9014	78.8985	104.7999	34.9712
700	27.2744	83.0736	110.3480	35.6596
800	28.3221	86.6413	114.9634	36.1155
900	29.2119	90.0506	119.2625	36.4431
1000	29.9237	93.0496	122.9733	36.6798
1100	30.5700	96.1115	126.6815	36.8603
1200	31.1077	98.8008	129.9085	37.0013
1300	31.5707	101.3474	132.9181	37.1110
1400	31.9564	103.5305	135.4869	37.1997
1500	32.3308	105.9775	138.3083	37.2712
1600	32.6418	108.1334	140.7752	37.3261
1700	32.9093	109.9722	142.8815	37.3757
1800	33.1505	111.9261	145.0766	37.4117
1900	33.3815	113.6332	147.0147	37.4489
2000	33.5893	115.4232	149.0125	37.4795

Tungsten hexafluoride

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	15.5523	58.4007	73.9530	23.8520
273.16	18.3070	63.6450	81.9520	27.7118
298.16	19.1706	65.3375	84.5081	28.7626
300	19.2072	65.4091	84.6163	28.8212
400	22.0030	71.3058	93.3088	31.8110
500	24.4623	77.0764	101.5387	33.7143
600	25.8589	81.1255	106.9844	34.7389
700	27.1752	85.1643	112.3395	35.4670
800	28.2293	88.8100	117.0393	35.9599
900	29.1364	92.3476	121.4840	36.3205
1000	29.8760	95.4555	125.3315	36.5874
1100	30.4458	98.0157	128.4615	36.7704
1200	31.0312	101.0268	132.0580	36.9324
1300	31.4608	103.3723	134.8331	37.0447
1400	31.8505	105.6323	137.4828	37.1403
1500	32.2156	107.9324	140.1480	37.2180
1600	32.5472	110.2466	142.7938	37.2829
1700	32.8187	111.8919	144.7106	37.3382
1800	33.0466	113.7847	146.8313	37.3773
1900	33.2835	115.4073	148.6908	37.4179
2000	33.4912	117.3472	150.8384	37.4483

Rhenium hexafluoride

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	15.4581	58.3207	73.7788	23.9925
273.16	18.3151	63.6185	81.9336	27.8360
298.16	19.1434	65.2234	84.3668	28.8753
300	19.2229	65.3828	84.6057	28.9637
400	22.0481	71.2808	93.3289	31.9129
500	24.1805	76.4007	100.5812	33.6625
600	25.8754	80.9950	106.8708	34.7772
700	27.1957	85.0814	112.2771	35.6131
800	28.2795	88.8902	117.1697	35.9863
900	29.1777	92.3228	121.5005	36.3468
1000	29.8943	95.3613	125.2556	36.5975
1100	30.4732	98.0896	128.5628	36.7820
1200	31.0324	100.7564	131.7888	36.9409
1300	31.5137	103.4845	134.9982	37.0618
1400	31.9308	105.9006	137.8314	37.1573
1500	32.2468	107.9225	140.1693	37.2269
1600	32.5677	110.0554	142.6231	37.2923
1700	32.8282	112.0632	144.8914	37.3386
1800	33.0601	113.5325	146.5926	37.3835
1900	33.3177	115.6636	148.9813	37.4234
2000	33.5218	117.1214	150.6432	37.4572

Osmium hexafluoride

T(°K)	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	14.7831	57.1297	71.9128	23.6509
273.16	17.7368	62.1956	79.9324	27.6712
298.16	18.6185	63.7864	82.4049	28.7382
300	18.6780	63.9012	82.5792	28.8055
400	21.6212	69.6956	91.3168	31.8336
500	23.8671	74.7889	98.6560	33.6386
600	25.5932	79.3096	104.9028	34.7493
700	26.9493	83.3227	110.2720	35.4797
800	28.0512	86.9743	115.0255	35.9823
900	28.9323	90.2916	119.2239	36.3241
1000	29.6871	93.4221	123.1092	36.5840
1100	30.3403	96.2939	126.6342	36.7857
1200	30.8790	98.9175	129.7965	36.9356
1300	31.3106	101.2240	132.5346	37.0455
1400	31.7877	104.1915	135.9792	37.1478
1500	32.1476	106.1503	138.2979	37.2267
1600	32.4455	108.1689	140.6144	37.2847
1700	32.7295	110.5382	142.8677	37.3378
1800	33.0097	112.1809	145.1906	37.3843
1900	33.1951	113.5522	146.7473	37.4175
2000	33.4184	115.3477	148.7661	37.4512

Irridium hexafluoride

$T(°K)$	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	14.8095	57.1554	71.9649	23.7634
273.16	17.7965	62.2446	80.0411	27.8169
298.16	18.6845	63.8397	82.5242	28.8905
300	18.7424	63.9426	82.6850	28.9514
400	21.7067	69.7728	91.4795	31.9574
500	23.9510	74.8806	98.8316	33.7280
600	25.6916	79.4315	105.1231	34.8331
700	27.0274	83.4400	110.4674	35.5336
800	28.1303	87.1086	115.2389	36.0274
900	29.0229	90.4379	117.4736	36.3690
1000	29.7751	93.5539	123.3290	36.6236
1100	30.4110	96.4592	126.8702	36.8132
1200	30.9517	99.0305	129.9822	36.9608
1300	31.3784	101.4112	132.7896	37.0663
1400	31.8505	104.1674	136.0179	37.1679
1500	32.1943	106.2251	138.4194	37.2398
1600	32.5246	108.4261	140.9507	37.3050
1700	32.7859	110.0215	142.8074	37.3507
1800	33.0522	112.2268	145.2790	37.3964
1900	33.2688	113.8387	147.1075	37.4320
2000	33.4687	115.5644	149.0331	37.4618

Platinum hexafluoride

$T(°K)$	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	15.1179	57.2923	72.4102	24.3157
273.16	18.1510	62.4767	80.6277	28.3179
298.16	19.0305	64.0757	83.1062	29.3431
300	19.1102	64.2176	83.3278	29.4238
400	22.0813	70.1386	92.2199	32.3163
500	23.9709	74.5244	98.4953	33.8896
600	26.0241	79.9042	105.9283	35.0354
700	27.3553	84.0341	111.3894	35.6952
800	28.4158	87.6920	116.1078	36.1482
900	29.2525	91.0181	120.2706	36.4660
1000	30.0656	94.3737	124.4393	36.7154
1100	30.6200	96.9863	127.6063	36.8793
1200	31.1653	99.8531	131.0184	37.0137
1300	31.6290	102.4147	134.0437	37.1226
1400	32.0232	104.6546	136.6778	37.2118
1500	32.3749	107.0555	139.4304	37.2758
1600	32.6716	108.4144	141.5850	37.3360
1700	32.9544	111.0994	144.0538	37.3799
1800	33.2167	112.9809	146.1976	37.4250
1900	33.4246	114.7238	148.1484	37.4562
2000	33.6338	116.5437	150.1775	37.4840

Uranium hexafluoride

$T(°K)$	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	17.5765	60.8668	78.4433	26.6560
273.16	20.5018	66.7938	87.2956	30.0956
298.16	21.3355	68.6003	89.9358	30.9620
300	21.4020	68.7644	90.1664	30.9801
400	24.1273	75.2887	99.4160	34.2159
500	26.1256	80.8699	106.9955	34.7797
600	27.6484	85.8222	113.4706	35.6055
700	28.8433	90.2032	119.0465	36.1474
800	29.7795	94.1135	123.8930	36.5032
900	30.5169	97.5619	128.0788	36.7478
1000	31.1015	100.9528	132.0543	36.9338
1100	31.6923	103.8955	135.5878	37.0719
1200	32.1667	106.7815	138.9482	37.1798
1300	32.5283	109.1355	141.6638	37.2627
1400	32.8596	111.4853	144.3449	37.3278
1500	33.1702	113.8590	147.0292	37.3831
1600	33.4327	115.9720	149.4047	37.4278
1700	33.6734	118.0953	151.7687	37.4648
1800	33.8918	120.2203	154.1121	37.4946
1900	34.0907	121.9644	156.0551	37.5236
2000	34.2580	123.7866	158.0446	37.5444

Neptunium hexafluoride

$T(°K)$	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	17.0369	60.0705	77.1074	26.3482
273.16	20.0446	65.8507	85.8953	29.9206
298.16	20.9295	67.6674	88.5969	30.8305
300	20.9736	67.7635	88.7371	30.8587
400	23.8113	74.2485	86.0598	33.3612
500	25.8573	79.6839	105.6412	34.7369
600	27.4071	84.6182	112.0253	35.5727
700	28.6110	88.8637	117.4747	36.1214
800	29.6052	92.9449	122.5501	36.4720
900	30.3567	96.3794	126.7361	36.7345
1000	30.9837	99.4116	130.3953	36.9217
1100	31.5624	102.7038	134.2662	37.0633
1200	32.0051	105.2053	137.2104	37.1722
1300	32.4320	107.9917	140.4237	37.2595
1400	32.7903	110.5107	143.3010	37.3274
1500	33.0655	112.5227	145.5882	37.3785
1600	33.3280	114.5452	147.8732	37.4232
1700	33.5683	116.5661	150.1344	37.4606
1800	33.7860	118.5726	152.3586	37.4910
1900	33.9967	120.6370	154.6337	37.5182
2000	34.1630	121.7946	155.9576	37.5401

Plutonium hexafluoride

$T(°K)$	$(H_0 - H_0^0)/T$	$-(F_0 - H_0^0)/T$	S^0	C_p^0
200	16.8660	59.8459	76.7119	26.3911
273.16	19.9478	65.5910	85.5388	30.0171
298.16	20.8305	67.3793	88.2098	30.9173
300	20.8760	67.4760	88.3506	30.9708
400	23.7360	73.9091	97.6451	33.4170
500	25.8251	79.4153	105.2404	34.8073
600	27.4048	84.3379	111.7427	35.6290
700	28.6116	88.6087	117.2203	36.1556
800	29.5774	92.4972	122.0746	36.5127
900	30.3520	95.9091	126.2611	36.7661
1000	31.0085	99.2220	130.2305	36.9449
1100	31.5342	102.0566	133.5908	37.0802
1200	32.0111	106.9138	136.9249	37.1858
1300	32.4308	107.6472	140.0780	37.2700
1400	32.7626	109.8869	142.6496	37.3348
1500	33.0736	112.1531	145.2267	37.3898
1600	33.3368	114.1532	147.4900	37.4344
1700	33.5981	116.4313	150.0294	37.4703
1800	33.8157	118.4227	152.2384	37.5005
1900	33.9731	120.0098	153.9829	37.5218
2000	34.1950	122.1544	156.3497	37.5478

values of thermodynamic quantities for uranium, neptunium, and plutonium hexafluoride show the same irregular order at every temperature which is due to the observed fundamental frequencies.

Experimental and calculated values for hexafluoride molecules in the gaseous state are compared in Table 3. Encluding the entropies of molybdenum and tungsten hexafluoride the agreement is excellent. The small disagreement in the entropy values for these molecules may be attributed to some error in the experimental observation of the molecular structural data. The good agreement between the experimental and spectroscopic values of thermodynamic quantities for some of the molecules studied here shows that the results presented here are very reliable and would be very useful in the future for the interpretation of the results of other experimental thermodynamic quantities and for the evaluation of normal frequencies in other related molecular systems having similar chemical bonds.

Table 3. Comparison of Experimental and Calculated Values (cal/deg mole).

Hexa-fluoride	Quantity	Experi-mental 298 °K	Ref.	Calculated (this work) 298.16 °K
Sulfur	S^0	69.5	41	69.7081
Tellurium	S^0	80.67	41	80.2385
Molybdenum	S^0	80.6*	42	83.8688
		80.05	19	
	C_p^0	28.35	19	28.7561
Tungsten	S^0	81.75	19	84.5081
	C_p^0	28.44	19	28.7626
Uranium	S^0	90.76	41	89.9358

* 298.15 °K.

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