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by

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STATISTICAL THERMODYNAMIC PROPERTIES OF HEXAFLUORIDE MOLECULES

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ABSTRACT

Useful statistical thermodynamic properties of fifteen octahedral hexafluorides are presented in graphical form. These include: vibrational partition function; populations of ν -lying vibrational states; densities of vibrational states; and cumulative vibrational population distributions. Values can be read directly from the graphs with an accuracy consistent with the accuracy of the experimental determinations of the vibrational fundamental frequencies, and the approximate validity of the harmonic oscillator approximation.

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I. INTRODUCTION

The purpose of this report is to present in the form of curves, and certain analytic expressions, some statistical thermodynamic properties of 15 hexafluoride molecules. Some of this data has been independently generated and used previously, e.g., Ref. 1. We feel that this reasonably comprehensive set of data will be useful as a reference and may eliminate some duplication of effort.

All of these curves are computer-generated using only the 15 fundamental vibrational frequencies. The frequencies used were taken from Ref. 2 and are presented in Table I for each of the molecules considered.

For each set of curves the corresponding section of this report details the manner in which they were generated. In the last section a few words are said about accuracy.

II. POPULATION OF LOW ENERGY VIBRATIONAL STATES

Each of the hexafluorides has 15 fundamental modes of vibration. However, since they have a two-fold and four three-fold degeneracies, it is sufficient to consider the six distinct frequencies $\omega_1, \dots, \omega_6$. Thus if $\omega'_1, \dots, \omega'_{15}$ are the 15 fundamental frequencies we have

$$\omega_1 = \omega'_1$$

$$\omega_2 = \omega'_2 = \omega'_3$$

and

$$\omega_i = \omega'_{3i-5} = \omega'_{3i-4} = \omega'_{3i-3},$$

for $i = 3, 4, 5, 6$.

Likewise if $V'_1, \dots, V'_{15}$ are the vibrational quanta in each of the 15 fundamental modes we use only the degenerate vibrational quanta $V_1, \dots, V_6$ where

$$V_1 = V'_1$$

$$V_2 = V'_2 + V'_3$$

and

$$V_i = V'_{3i-5} + V'_{3i-4} + V'_{3i-3}$$

for $i = 3, 4, 5, 6$.

Hence, for each vibrational state $V_1, \dots, V_6$ the degeneracy factor

$$D = (V_2 + 1) \prod_{i=3}^6 \frac{(V_i + 1)(V_i + 2)}{2}$$

yields the number of vibrational states which have the degenerate vibrational state $V_1, \dots, V_6$. For convenience we will refer to the degenerate

vibrational state as the vibrational state or sometimes merely as the state of a molecule.

Now for a fixed vibrational state $V_1, \dots, V_6$ let $F(T)$ be the fraction of molecules, at temperature T , which are in that state. Then $F(T)$ is given by

$$F(T) = D \frac{e^{-\frac{\sum \omega_i V_i}{kT}}}{Z(T)},$$

where $Z(T)$ is the partition function, as defined in the next section, and k is the Boltzmann constant.

In Figs. 1 through 15 $F(T)$ is plotted for 10, 11, or 12 highly populated vibrational states for each of the hexafluorides considered.

Notice that the reduced vibrational states do not always represent the most populated states. For example, the state (0,0,0,0,0,3) is never plotted but, for a few molecules, is more highly populated than the states which are plotted.

III. THE PARTITION FUNCTION, $Z(T)$

Let $d_1, \dots, d_6$ be the degeneracy factors for the hexafluorides. Thus, we see from the previous section that

$$d_1 = 1$$

$$d_2 = 2$$

and

$$d_i = 3$$

for $i = 3, 4, 5, 6$.

Now the definition of the partition function is given by

$$Z(T) = \sum D e^{-\frac{E}{kT}}$$

where the sum is taken over all vibrational states ($V_1, \dots, V_6$) and for each state D is the degeneracy and E is the vibrational energy defined as

$$E = \sum_{i=1}^6 \omega_i V_i.$$

The reader is referred to the previous section for the definition of D and "vibrational state."

Physically the function $Z(T)$ is proportional to the number of molecules per unit volume in a population of molecules having temperature T .

It is well known that the sum which defines $Z(T)$ can be carried out analytically to yield

$$Z(T) = \prod_{i=1}^6 \left(1 - e^{-\frac{\omega_i}{kT}} \right)^{-d_i}.$$

This expression was used to calculate $Z(T)$ and the resulting curves are presented in Figs. 16 through 19 for each of the 15 hexafluorides and for $0 \leq T \leq 350^\circ\text{K}$. For convenience $Z(T)$ is plotted for two temperature scales.

IV. DENSITY OF VIBRATIONAL STATES

A number of attempts have been made at finding simple approximations to the number of vibrational states with energy in a given energy range. The mathematical approach has been to try and find general formulas which depend only on the ω_i , e.g., Ref. 3. Physical scientists have tended to include in their approximations one or more parameters, besides the ω_i , which are determined by best fit to actual data for each molecule, e.g., Ref. 4.

The second approach requires more computation and yields better results, especially when the energy range of interest is limited. We have chosen the second approach but have used a different functional form than those appearing in the literature. A computer-generated count of the states was made and the fit is to this data for $0 \leq E \leq 5000 \text{ cm}^{-1}$ for each of the hexafluoride molecules in Table I. The functional form used is not asymptotically correct as E goes to infinite and hence should not be used for energies greater than 5000 wavenumbers (cm^{-1}). However, for these molecules and for temperatures of no more than 400 K only a small fraction of the population has energy greater than 5000 cm^{-1} .

Define $N(E)$ by

$$N(E) = \sum D \{ (V_1) : 0 \leq \omega_1 V_1 + \dots + \omega_6 V_6 \leq E \}$$

where, as indicated, the sum is over all vibrational states of energy not greater than E , and D is the degeneracy of each state as defined in Section II. For $0 \leq E \leq 5000 \text{ cm}^{-1}$ we used a least-squares cubic fit to the curve $\ln N(E)$ vs $\ln E$. Thus we have

$$\ln N(E) \approx P_3(\ln E)$$

where

$$P_3(X) = b_1 X^3 + b_2 X^2 + b_3 X + b_4.$$

The coefficients of P_3 , which were found for each molecule are presented in Table II.

Now the derivative of $N(E)$ is, of course, either zero or undefined for each value of E because $N(E)$ is a step function. However, we write $N'(E)$ to mean the average number of states per cm^{-1} in a small interval (say 100 cm^{-1}) centered at E . Hence, for the density of vibrational states $g(E) = N'(E)$ we use

$$g(E) = \left(\frac{P'_3(\ln E)}{E} \right) e^{P_3(\ln E)}$$

where P'_3 is the derivative of the polynomial P_3 .

We use this equation to compute $g(E)$ and the results are presented in Figs. 20 through 25. For convenience $g(E)$ is plotted for two energy scales.

V. CUMULATIVE POPULATION DISTRIBUTION

For a population of molecules at temperature T let $G(E, T)$ be the fraction of the molecules which have energy less than or equal to E . Then if $g(E)$ is the density of states function we have

$$G(E, T) = \int_0^E g(y) e^{-\frac{y}{kT}} dy.$$

$G(E, T)$ was calculated using this equation where the function g is defined in terms of a cubic polynomial as discussed in the previous section.

For each of the hexafluorides we plot $G(E, T)$ as a function of E for values of T from 200 K to 400 K in increments of 20 K. The results are presented in Figs. 26 through 33, where the top curve in each figure represents the distribution for $T = 200$ K the next for $T = 220$ K and the bottom for $T = 400$ K.

VI. ACCURACY

The main sources of inaccuracy in these curves are due to three factors. The first source of error is the value used for the fundamental frequencies. The second is the model, which considers only vibrational states. Also we use only first order terms in the vibrational quantum numbers to define energy. The third is the quality of the analytic fit to the vibrational states distribution in energy.

No systematic study of quality of the analytic fit was made. We merely chose a sample of data points and compared the plotted data to the data from actual counting of states.

The density of states curves for $E \geq 1600 \text{ cm}^{-1}$ are rarely off by 5% or more. For SF_6 the fit is not this good unless we restrict to $E \geq 2000 \text{ cm}^{-1}$ and for most less stiff molecules it is sufficient to require $E \geq 1000 \text{ cm}^{-1}$. The fit is poor for $E < 1000 \text{ cm}^{-1}$ in almost all cases.

For the cumulative population distribution curves errors of 5% or more are very rare while errors of 3% are common over the entire range plotted.

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TABLE 1

FUNDAMENTAL FREQUENCIES OF HEXAFLUORIDE MOLECULES
IN THE VAPOR (cm^{-1})
(data from Ref. 2)

Molecule	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
SF_6	773.5	641.7	959.0	614.0	525.0	547.0
SeF_6	706.9	658.7	780.0	437.0	405.0	264.0
TeF_6	697.1	670.3	752.0	325.0	314.0	197.0
MoF_6	741.5	651.6	741.1	264.0	318.0	116.0
TcF_6	712.9	639.0	748.0	265.0	297.0	145.0
RuF_6	675.0	624.0	735.0	275.0	283.0	186.0
RhF_6	634.0	595.0	724.0	283.0	269.0	192.0
WF_6	771.0	677.2	711.0	258.0	320.0	127.0
ReF_6	753.7	671.0	715.0	257.0	295.0	147.0
OsF_6	730.7	688.0	720.0	268.0	276.0	205.0
IrF_6	701.7	645.0	719.0	276.0	267.0	206.0
PtF_6	656.4	601.0	705.0	273.0	242.0	211.0
UF_6	667.1	532.5	624.0	186.2	202.0	142.0
NpF_6	654.0	535.0	624.0	198.6	208.0	164.0
PuF_6	628.0	525.0	616.0	206.0	211.0	173.0

TABLE 11

COEFFICIENTS OF THE CUBIC POLYNOMIALS P_3

$$\ln N(\lambda) = P_3(\ln \lambda)$$

$$P_3(X) = b_4 X^3 + b_2 X^2 + b_3 X + b_1$$

$$E(\text{cm}^{-1})$$

Molecule	b_1	b_2	b_3	b_4
Si ₆	0.15056	-1.9765	9.5555	-17.504
SeI ₆	0.14046	-1.6989	7.5691	-15.463
TeI ₆	0.12723	-1.5908	5.7615	-9.5049
MoI ₆	0.11249	-1.0925	4.1134	-6.1866
TeI ₆	0.12446	-1.5480	5.8897	-10.595
RuI ₆	0.13528	-1.5189	6.8919	-12.717
RhI ₆	0.12921	-1.4206	6.1515	-10.957
WI ₆	0.12011	-1.2557	5.2564	-8.9687
ReF ₆	0.12407	-1.5357	5.7791	-10.267
OsF ₆	0.13456	-1.5530	7.1392	-13.553
IrI ₆	0.13522	-1.5607	7.1643	-13.550
PtI ₆	0.12624	-1.3567	5.7394	-10.144
UI ₆	0.12589	-1.5479	6.2818	-12.554
NpF ₆	0.11461	-1.0914	4.2466	-7.4126
PuI ₆	0.11842	-1.4609	4.6121	-8.0859

Fig. 1 Population of low-energy vibrational states of SF_6

Fig. 2 Population of low-energy vibrational states of SeF₆

Fig. 3 Population of low-energy vibrational states of TeF₆

Fig. 4 Population of low-energy vibrational states of MoF_6

Fig. 5 Population of low-energy vibrational states of TcF_6

Fig. 6 Population of low-energy vibrational states of RuF_6

Fig. 7 Population of low-energy vibrational states of RhF_6

Fig. 8 Population of low-energy vibrational states of WF₆

REF6

Fig. 9 Population of low-energy vibrational states of ReF_6

Fig. 10 Population of low-energy vibrational states of OsF₆

Fig. 11 Population of low-energy vibrational states of IrF_6

Fig. 12 Population of low-energy vibrational states of PtF_6

Fig. 13 Population of low-energy vibrational states of UF₆

Fig. 14 Population of low-energy vibrational states of NpF_6

Fig. 15 Population of low-energy vibrational states of PuF_6

Fig. 16 Vibration partition function for UF₆, NpF₆, MoF₆, TcF₆, RhF₆, OsF₆, TeF₆, SF₆

Fig. 17 Vibration partition function for PuF_6 , WF_6 , ReF_6 , RuF_6 , PtF_6 , IrF_6 , SeF_6

Fig. 18 Vibration partition function for UF_6 , NpF_6 , MoF_6 , TcF_6 , RhF_6 , OsF_6 , TeF_6 , SF_6

Fig. 19 Vibration partition function for PuF_6 , WF_6 , ReF_6 , PtF_6 , RuF_6 , IrF_6 , SeF_6

Fig. 20 Density of vibrational states for WF_6 , TcF_6 , PtF_6 , OsF_6 , SeF_6

Fig. 21 Density of vibrational states for MoF_6 , ReF_6 , RhF_6 , TeF_6 , SF_6

Fig. 22 Density of vibrational states for UF_6 , NpF_6 , PuF_6 , RuF_6 , IrF_6

Fig. 23 Density of vibrational states for WF_6 , TcF_6 , PtF_6 , OsF_6 , SeF_6

Fig. 24 Density of vibrational states for MoF_6 , ReF_6 , RhF_6 , TeF_6 , SF_6

Fig. 25 Density of vibrational states for UF_6 , NpF_6 , PuF_6 , RuF_6 , IrF_6

Fig. 26 Cumulative population distribution for SF_6 and SeF_6
 $T = 200$ (20) 400 K

Fig. 27 Cumulative population distribution for TeF_6 and MoF_6
 $T = 200$ (20) 400 K

Fig. 28 Cumulative population distribution for TcF_6 and RuF_6
 $T = 200 \text{ (20) } 400 \text{ K}$

Fig. 29 Cumulative population distribution for RhF₆ and WF₆
T = 200 (20) 400 K

Fig. 30 Cumulative population distribution for ReF_6 and OsF_6
 $T = 200 \text{ (20) } 400 \text{ K}$

Fig. 31 Cumulative population distribution for IrF_6 and PtF_6
 $T = 200$ (20) 400 K

Fig. 32 Cumulative population distribution for UF_6 and NpF_6
 $T = 200 \text{ (20) } 400 \text{ K}$

Fig. 33 Cumulative population distribution for PuF_6
 $T = 200 \text{ (20) } 400 \text{ K}$