Thermodynamic Functions of Element 105 in Neutral and Ionized States

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The basic thermodynamic functions, the entropy, free energy, and enthalpy, for element 105 (hahnium) in electronic configurations d^3s^2, d^3sp, and d^4s^1 and for its +5 ionized state ($5f^{14}$) have been calculated as a function of temperature. The data are based on the results of the calculations of the corresponding electronic states of element 105 using the multiconfiguration Dirac–Fock method.

I. Introduction

During recent years there has been a considerably growing interest in the physics and chemistry of the transactinide elements. Elements 104 and 105 and their halides have been studied both experimentally[1-4] and theoretically.[5-7] An extensively used method for experimental investigations of the properties of these elements is thermal gas chromatography. With this technique, data on the volatility of element 104 in comparison with its analogs, Zr and Hf, have been obtained[3] and the volatility of element 103 as a possible analog of Tl has been investigated.[8] The gas chromatography has been applied as well to the investigation[1-4] of the volatility of chlorides and bromides of elements 104 and 105 along with their analogs, Zr/Hf and Nb/Ta, respectively.

An important aspect of the study was the investigation of the physicochemical properties of the heavy elements as a function of electronic configuration. A number of experiments[8,9] were carried out to study the volatility of the elements depending on their electronic configurations, and theoretical estimations of the sublimation enthalpy of element 104 as a function of electronic configuration have been done in ref 10 using some correlations.

Estimations of the sublimation enthalpy for transactinide elements are of importance for the gas chromatography experiments. Besides, the more complete study of the physics and chemistry of the transactinide elements should include the knowledge of their thermodynamic functions, especially as a function of temperature. From the thermodynamic data it is possible to predict the chemical behavior.

The calculation of thermodynamic data, when no experimental data exist, is possible using spectroscopic levels of the gaseous atoms. Provided the latter are not known from experiment, they can be calculated using relativistic atomic codes. Thus, in this work we present the basic thermodynamic functions, S, G, and H, for element 105, in different electronic configurations as a function of temperature, which were calculated using the energy levels obtained from the multiconfiguration Dirac–Fock (MCDF) calculations. These calculations were performed for the ground-state electronic configuration of element 105 $d^3s^2(^4F)$, as well as for the excited-state electronic configurations, $d^3sp(^6G)$ and $d^4s(^6D)$. The sublimation enthalpy of the metallic hahnium has been estimated using the MCDF atomic data.

TABLE 1: Calculated Relative Energy Eigenvalues for the Lowest Energy State That Is Dominated by the $d^3s^2(^4F)$ Configuration as a Function of Total Angular Momentum J for V, Nb, Ta, and Ha

element	angular momentum and parity	energy (eV)	energy (cm⁻¹)	exptl[11] energy^a (cm⁻¹)
V	$^3/_2+$	0.0	0.0	0.0
	$^5/_2+$	0.0161	129.85	137.38
	$^7/_2+$	0.0386	311.31	323.42
	$^9/_2+$	0.0665	536.32	553.02
Nb	$^3/_2+$	0.0	0.0	0.0
	$^5/_2+$	0.0525	423.41	444.11
	$^7/_2+$	0.1204	971.03	1011.32
	$^9/_2+$	0.1965	1584.77	1662.57
Ta	$^3/_2+$	0.0	0.0	0.0
	$^5/_2+$	0.2034	1640.42	2010.10
	$^7/_2+$	0.4255	3431.66	3963.92
	$^9/_2+$	0.6399	5160.79	5621.04
Ha	$^3/_2+$	0.0	0.0	0.0
	$^5/_2+$	0.4571	3686.71	(4746.25)
	$^7/_2+$	0.8264	6665.28	(8149.68)
	$^9/_2+$	1.0966	8844.56	(10011.08)

^{a} For Ha the data are normalized and extrapolated to the experimental values for V, Nb, and Ta.

Results of the present MCDF computations and the thermodynamic data calculated from them are presented in the next sections.

II. Results of the MCDF Calculations

The MCDF calculations[5b] have shown the ground-state electronic configuration of Ha to be $d^3s^2(^4F)$. The present calculations show that the next excited states are $d^3sp(^6G)$ and $d^4s^1(^6D)$, lying at 1.9(±0.4) and 2.0(±0.4) eV higher in energy, respectively. The energies of the lowest energy states that are dominated by the $d^3s^2(^4F)$, $d^3sp(^6G)$, and $d^4s^1(^6D)$ configurations as a function of the total angular momentum quantum number J for hahnium along with its group-5 analogs are presented in Tables 1–3.

Since the MCDF method does not give the excitation energies as accurately as desired (mainly due to the influence of the core polarization, which cannot be taken into account by the program), the accuracy of the results has been increased by using an extrapolation procedure to obtain "experimental" energies. The extrapolation procedure used is based on ideas from the finite difference method in numerical analysis[12] and is described in

TABLE 2: Calculated Relative Energy Eigenvalues for the Lowest Energy States That Is Dominated by the $d^4s(^6D)$ Configuration as a Function of Total Angular Momentum J for V, Nb, Ta, and Ha

element	angular momentum and parity	energy (eV)	energy (cm^{-1})	exptl[11] energy[a] (cm^{-1})
V	$^1/_2+$	0.0	0.0	0.0
	$^3/_2+$	0.0053	42.67	40.88
	$^5/_2+$	0.0140	112.92	107.81
	$^7/_2+$	0.0253	204.23	199.24
	$^9/_2+$	0.0369	297.86	312.57
Nb	$^1/_2+$	0.0	0.0	0.0
	$^3/_2+$	0.0163	131.47	154.19
	$^5/_2+$	0.0423	341.17	391.99
	$^7/_2+$	0.0763	615.39	695.25
	$^9/_2+$	0.1148	925.91	1050.26
Ta	$^1/_2+$	0.0	0.0	0.0
	$^3/_2+$	0.0311	250.84	216.84
	$^5/_2+$	0.1361	1097.71	1484.66
	$^7/_2+$	0.2301	1855.86	2475.79
	$^9/_2+$	0.3585	2891.46	3592.48
Ha	$^1/_2+$	0.0	0.0	0.0
	$^3/_2+$	0.1480	1193.68	(1022.64)
	$^5/_2+$	0.3530	2847.10	(3851.03)
	$^7/_2+$	0.5510	4444.06	(6060.04)
	$^9/_2+$	0.7330	5911.97	(7656.90)

[a] The data for Ha are extrapolated and normalized to the experimental data for V, Nb, and Ta.

TABLE 3: Calculated Relative Energy Eigenvalues for the Lowest Energy State That Is Dominated by the $d^3sp(^6G)$ Configuration as a Function of Total Angular Momentum J for V, Nb, Ta, and Ha

element	angular momentum and parity	energy (eV)	energy (cm^{-1})	exptl[11] energy[a] (cm^{-1})
V	$^3/_2-$	0.0	0.0	0.0
	$^5/_2-$	0.0102	82.26	88.40
	$^7/_2-$	0.0245	197.93	211.09
	$^9/_2-$	0.0429	345.99	367.30
	$^{11}/_2-$	0.0654	527.45	555.70
	$^{13}/_2-$	0.0920	741.98	774.99
Nb	$^3/_2-$	0.0	0.0	0.0
	$^5/_2-$	0.0353	284.69	309.01
	$^7/_2-$	0.0837	675.04	631.96
	$^9/_2-$	0.1448	1167.81	1265.26
	$^{11}/_2-$	0.2176	1754.94	1763.14
	$^{13}/_2-$	0.3015	2431.59	2204.46
Ta	$^3/_2-$	0.0	0.0	0.0
	$^5/_2-$	0.1450	1169.43	1793.80
	$^7/_2-$	0.3396	2738.87	3175.61
	$^9/_2-$	0.5705	4601.08	5297.06
	$^{11}/_2-$	0.8378	6756.86	7624.18
	$^{13}/_2-$	1.1521	9291.69	
Ha	$^3/_2-$	0.0	0.0	0.0
	$^5/_2-$	0.3730	3008.25	(4814.81)
	$^7/_2-$	0.7360	5935.84	(7386.73)
	$^9/_2-$	0.9440	7613.36	(9429.60)
	$^{11}/_2-$	1.4440	11645.86	(14250.86)
	$^{13}/_2-$	2.6540	21404.50	

[a] For Ha the data are normalized and extrapolated to the experimental values for V, Nb, and Ta.

application to elements 104 and 105 in refs 5a,b. The uncertainty in the ionization potentials presented there is less than 0.3 eV. These experimental values, shown in Tables 1–3 in the parentheses, can be used for calculations of the thermodynamic functions and predictions of chemical properties.

A general trend in the group is an increase in energies (more negative) of the excited states in going from V to Ha. The first fine-structure level ($J = ^5/_2$) for Ha (d^3s^2) has an energy which is nearly enough to bring Ta to the next excited state (^4P). Thus, much higher temperatures are needed to make the excited states of Ha occupied in comparison with the analogs.

III. Thermodynamic Functions and Sources of Data

A model of a monatomic ideal gas was used to calculate the entropy, enthalpy, and free energy of hahnium. The expression for the translational entropy of an ideal gas is

$$S = N_0 k \left[\ln\left(\frac{Z(2\pi mkT)^{3/2}kT}{h^3 P} \right) + \frac{5}{2} \right] \quad (1)$$

Here $N_0 = 6.022 \times 10^{23}$ mol^{-1}, $k = 1.380 \times 10^{-23}$ J $\times$ K^{-1}, $P = 1$ atm $= 1.013\,25 \times 10^6$ dyne cm^{-1}; m is the mass of Ha equal to $266/N_0$, and $h = 6.626 \times 10^{-34}$ J s. The calculation of this function, as well as of the free energy, for an ideal gas requires a calculation of the specific form of the partition function Z, i.e.

$$Z_i = \sum_k g_k e^{-\Delta\epsilon_k/T} = \sum_J (2J + 1)e^{-\Delta\epsilon_J/T} \quad (2)$$

Here g_k is a statistical weight for electron states (or degree of degeneracy of a level) equal to $2J + 1$, and $\Delta\epsilon_J$ is the difference between energies of the fine-structure components for a given term of the element. The summation is taken over all possible values of the total angular momentum J for all L and S states.

Considering the monatomic gas in a temperature interval between 273 and 4000 K, we make here the following comment. As the gas temperatures increase, the number of atoms in excited states also increases with some of them even being ionized. When the temperatures are not too high ($T \ll I_{ion}$), the relative number of ionized atoms in the gas phase is negligible, but the gas is nearly fully ionized at temperatures of the order of the ionization energy and not only at $T \gg I_{ion}$.[13] Thus, a nonionized gas can be considered at temperatures $T \ll I_{ion}$.

In many atoms the energy difference between the ground state (term) and the first excited state (next term) is comparable with the ionization energy. At temperatures $T \ll I_{ion}$, the gas will therefore be practically free not only of ionized atoms but also of excited atoms, so all the atoms may be regardered as being in the ground state.

The temperatures (below 5000 K), for which the thermodynamic data are presented, are below the boiling point of Ha (for comparison, T_b of Nb is 5200 K and T_b of Ta is 5702 K). Thus, at the temperatures below 5000 K Ha will be in the lowest energy state ^4F of the electronic configuration d^3s^2. The partition function Z in this case can be very well calculated only for the ^4F state using the fine-structure energy levels from Table 1. The next ionized state of the d^3s^2 configuration, probably, ^4P, will be at energies higher than 10 011.08 cm^{-1} (the highest level of the ^4F term). Taking this value as a limit, we calculated a value of Z for the ^4P term at 4000 K. This correction to the value of Z obtained only for the ^4F term is 0.03. Thus, within the temperatures between 273 and 4000 K we can restrict ourselves to consideration of only the ^4F term. With the energy differences $\Delta\epsilon_J$ from Table 1, the expression for the partition function of Ha in the electronic configuration d^3s^2 as a function of temperature is

$$Z(\text{Ha}, d^3s^2) = 4 + 6e^{-4746/T} + 8e^{-8149/T} + 10e^{-10011/T} \quad (3)$$

The values of Z obtained for the d^3s^2 configuration and corresponding values of the entropy are given in Table 4.

We have also calculated the partition function and entropy for the next excited-state electronic configurations $d^3sp(^6G)$ and $d^4s(^6D)$, assuming the gas was previously ionized. Substitution of $\Delta\epsilon_J$ in eq 2 by their values from Tables 2 and 3 gives the following expressions for the partition function:

$$Z(\text{Ha}, d^3sp) = 4 + 6e^{-4815/T} + 8e^{-7387/T} + 10e^{-9429/T} +$$
$$12e^{-14251/T} + 14e^{-21404/T} \quad (4)$$

$$Z(\text{Ha}, d^4s^1) = 2 + 4e^{-1023/T} + 6e^{-3851/T} + 8e^{-6060/T} +$$
$$10e^{-7657/T} \quad (5)$$

where T is measured in cm^{-1}.

TABLE 4: Calculated Electron Partition Function Z and the Entropy S for Element 105 in Electronic Configuration d³s²(⁴F)

T (K)	(cm⁻¹)	Z	ln Z	S (J mol⁻¹ K⁻¹)
273	189	4.000	1.386	188.05
298	206	4.000	1.386	189.90
323	224	4.000	1.386	191.56
373	259	4.000	1.386	194.54
423	293	4.000	1.386	197.17
500	346	4.000	1.386	200.63
750	519	4.003	1.387	209.08
1000	695	4.006	1.387	215.05
1500	1038	4.065	1.402	223.61
2000	1390	4.200	1.435	229.86
2500	1731	4.460	1.495	234.99
3000	2085	4.856	1.580	239.49
3500	2423	5.288	1.666	243.40
4000	2780	5.788	1.756	246.93
$T \gg \Delta\epsilon_J$	$T \gg \Delta\epsilon_J$	28	3.332	>286.78

TABLE 5: Calculated Electron Partition Function Z and the Entropy S for Element 105 in Electronic Configuration d³sp(⁶G)

T (K)	(cm⁻¹)	Z	ln Z	S (J mol⁻¹ K⁻¹)
273	189	4.000	1.386	188.05
298	206	4.000	1.386	189.90
323	224	4.000	1.386	191.56
373	259	4.000	1.386	194.54
423	293	4.000	1.386	197.17
500	346	4.000	1.386	200.63
750	519	4.003	1.387	209.08
1000	695	4.006	1.387	215.05
1500	1038	4.065	1.402	223.61
2000	1390	4.239	1.444	229.91
2500	1731	4.530	1.511	235.14
3000	2085	4.949	1.599	239.66
3500	2423	5.441	1.694	243.65
4000	2780	6.039	1.798	247.30
$T \gg \Delta\epsilon_J$	$T \gg \Delta\epsilon_J$	30	3.401	>281.74

TABLE 6: Calculated Electron Partition Function Z and the Entropy S for Element 105 in Electronic Configuration d⁴s¹(⁶D)

T (K)	(cm⁻¹)	Z	ln Z	S (J mol⁻¹ K⁻¹)
273	189	2.016	0.701	182.36
298	206	2.028	0.707	184.23
323	224	2.041	0.714	185.98
373	259	2.077	0.731	189.09
423	293	2.122	0.752	191.90
500	346	2.207	0.792	195.69
750	519	2.557	0.939	205.36
1000	695	2.943	1.079	212.42
1500	1038	3.677	1.302	222.77
2000	1390	4.388	1.479	230.22
2500	1731	5.230	1.655	236.32
3000	2085	6.088	1.806	241.37
3500	2423	6.933	1.936	245.66
4000	2780	7.805	2.055	249.42
$T \gg \Delta\epsilon_J$	$T \gg \Delta\epsilon_J$	54	3.959	>310.82

The values obtained for Z and corresponding values of the entropy for P = 1 atm are presented in Tables 5 and 6.

For the heavy-metal vapors, sometimes in practice a range of high temperatures is of importance, so that the temperature is large in comparison with the fine-structure intervals, $T \gg \Delta\epsilon_J$. In this case, one can put $e^{-\Delta\epsilon_J/T} \simeq 1$ in expression 2, and Z becomes simply the total number of the fine-structure components (2S + 1)(2L + 1). In this case the value of specific heat becomes constant ($C_v = \,^3/_2$) (see ref 12). Thus, at $T \gg \Delta\epsilon_J$, the values of Z for Ha in electronic configurations d³s², d³sp, and d⁴s are 28, 30, and

TABLE 7: Calculated Values of the Free Energy, G, and the Enthalpy, H, for Element 105 in Electronic Configuration d³s²(⁴F)

T (K)	TS (kJ mol⁻¹)	−G (kJ mol⁻¹)	H (kJ mol⁻¹)
273	51.338	45.664	5.673
298	56.582	50.388	6.194
323	61.873	55.159	6.714
373	72.564	64.811	7.753
423	83.402	74.610	8.792
500	100.315	89.922	10.393
750	156.810	141.220	15.590
1000	215.053	194.267	20.786
1500	335.408	304.229	31.179
2000	459.713	418.140	41.572
2500	587.475	535.510	51.965
3000	718.464	656.106	62.358
3500	851.913	779.161	72.751
4000	987.725	904.581	83.144

TABLE 8: Calculated Values of the Free Energy, G, and the Enthalpy, H, for Element 105 in Electronic Configuration d³sp(⁶G)

T (K)	TS (kJ mol⁻¹)	−G (kJ mol⁻¹)	H (kJ mol⁻¹)
273	51.338	45.664	5.673
298	56.582	50.388	6.194
323	61.873	55.159	6.714
373	72.564	64.811	7.753
423	83.402	74.610	8.792
500	100.315	89.922	10.393
750	156.810	141.220	15.590
1000	215.053	194.267	20.786
1500	335.408	304.229	31.179
2000	459.820	418.320	41.500
2500	587.850	535.885	51.965
3000	718.980	656.634	62.346
3500	852.775	780.052	72.723
4000	989.200	906.048	83.152

TABLE 9: Calculated Values of the Free Energy, G, and the Enthalpy, H, for Element 105 in Electronic Configuration d⁴s¹(⁶D)

T (K)	TS (kJ mol⁻¹)	−G (kJ mol⁻¹)	H (kJ mol⁻¹)
273	49.781	44.107	5.673
298	54.898	48.706	6.194
323	60.071	53.357	6.714
373	70.529	62.776	7.753
423	81.542	72.749	8.792
500	97.843	87.449	10.393
750	154.020	138.430	15.590
1000	212.488	191.703	20.786
1500	334.151	302.972	31.179
2000	460.441	418.868	41.572
2500	590.802	538.836	51.965
3000	724.112	661.754	62.358
3500	859.808	787.056	72.751
4000	997.666	914.521	83.144

54, respectively. The corresponding values of the entropy are presented in Tables 4–6.

The free energy for element 105 has been calculated using the formula

$$G = -N_0 kT \left[\ln\left(\frac{Z(2\pi mkT)^{3/2} kT}{h^3 P} \right) \right] \qquad (6)$$

The calculated G's for Ha(d³s²), Ha(d³sp), and Ha(d⁴s¹) as a function of temperature are given in Tables 7–9.

The enthalpy, H, can be calculated from the general expression

$$G = H - TS \qquad (7)$$

The values obtained for H for the Ha states under discussion are also presented in Tables 7–9.

A Ha⁵⁺ ionized state was also included in the present consideration. For the 5f¹⁴ electronic configuration the value of

TABLE 10: Calculated Values of the Entropy, S, the Free Energy, G, and the Enthalpy, H, for $Ha^{5+}(5f^{14})^a$

T		S	TS	$-G$	H
(K)	(cm⁻¹)	(J mol⁻¹ K⁻¹)	(kJ mol⁻¹)	(kJ mol⁻¹)	(kJ mol⁻¹)
273	189	176.53	48.191	42.517	5.673
298	206	178.38	53.182	46.982	6.205
323	224	180.04	58.153	51.439	6.714
373	259	183.02	62.266	60.513	5.523
423	293	185.65	78.529	69.736	8.793
500	346	189.13	94.562	84.169	10.393
750	519	197.55	148.162	132.586	15.576
1000	695	203.53	203.535	182.748	20.781
1500	1038	211.96	317.942	286.759	31.179
2000	1390	217.94	435.889	394.275	41.618
2500	1731	222.58	556.451	504.485	51.965
3000	2085	226.37	679.113	616.725	62.387
3500	2423	229.56	803.445	730.689	72.751
4000	2780	232.33	929.316	846.172	83.144

^{a} For $Ha^{5+}(5f^{14})$, $Z = 1$.

TABLE 11: Approximate Solid-State Electronic Configurations of the Transition Metals of Groups 4–7

group 4	group 5	group 6	group 7
Ti $d^{3-x}sp^x$	V d^4s	Cr d^5s	Mn $d^6s + d^5sp$
Zr $d^{3-x}sp^x$	Nb d^4s	Mo d^5s	Tc $d^{6-x}sp^x$
Hf $d^{3-x}sp^x$	Ta $d^{4-x}sp^x$	W d^5s	Re $d^{6-x}sp^x$
104 $d^{3-x}sp^x$	105 $d^{4-x}sp^x$	106 d^5s	107 $d^{6-x}sp^x$

Z is equal to unity. The calculated thermodynamic values for Ha^{5+} are presented in Table 10.

The values of the partition function can also be used for calculating some other physicochemical characteristics such as, for example, chemical potentials. The latter can be used for calculations of a partial pressure of the gaseous element.

IV. Sublimation Enthalpies of the Metals

A. Electronic Structure of the Transition Metals. It was shown[14] that the highly directional properties of the d-electrons determine the crystal structure for transition metals. The following correlation has been accepted for the transition metals (see Table 11):

1. For metals which are likely to have electronic configuration d^x ($0 < x < 2$), the crystal lattice has the fcc structure.

2. For metals with d^5 configuration (at or near it), the crystal structure is bcc.

3. For metals with intermediate configurations d^x ($2 < x < 4$), the crystal lattice is hcp.

V, Nb, Ta, and Ha belong to the third class. It means that the lattice may change the symmetry from bcc to hcp depending on the temperature.

Our molecular orbital calculations[7] of hahnium compounds show that there is some electron population of the $7p_{1/2}$ orbitals of Ha. Analogously, we can assume that in the metallic hahnium as well as in metallic elements 106–111 the np electrons are available.

Metals of group 4 have $d^{3-x}sp^x$ configuration with x approximately equal for Ti and Zr and much larger for Hf. The presence of the p-electrons in the electronic configuration of Hf stabilizes the hcp structure. Hf transforms to the high-temperature bcc state at a very high temperature. Apparently, element 104 will be preferentially in the hcp structure too. But if consideration is taken of the fact that in the ground state the 7p orbitals of element 104 have a large electron population,[15,16] the hcp → fcc transformation is to be expected at higher temperatures.
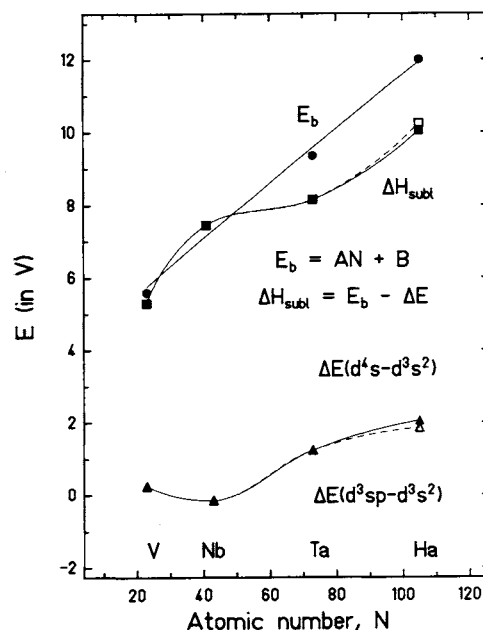

Figure 1. Sublimation energy of a metal ΔH_{subl}, cohesive energy E_c, and the difference between energies of electronic configurations in the gas phase and in the solid state $\Delta E(d^4s-d^3s^2)$ (filled triangles) and $\Delta E(d^3sp-d^3s^2)$ (open triangle for Ha) as a function of the atomic number. A filled square is ΔH_{subl} of Ha for the electronic configuration d^4s in the metal, and an open square is ΔH_{subl} for the d^3sp electronic configuration.

In group 5, Ta and Ha can be considered a borderline case on the bcc side of the border.

In group 6 the p-valence electrons are high in energy owing to a strong orbital effect in the half-occupied d^5 shell. This requires a bcc structure.

For metallic Tc and Re a larger population of the p-atomic orbitals was accepted[14] in comparison with Nb and Ta, and the $d^{6-x}sp^x$ configuration was considered as an equivalent to the $d^{4+x}sp^x$ one. This would stabilize the hcp structure in all three metals of the group (Tc, Re, and element 107), with the effect being more pronounced in the case of element 107 due to strong relativistic effects.

B. Sublimation Enthalpy of the Metallic Hahnium. Assuming that hahnium has the same structure in the metallic state as Nb or Ta having the bcc lattice, we will try to estimate its sublimation enthalpy using the results of the present MCDF calculations. The sublimation enthalpy can be expressed[17] as

$$\Delta H_{subl} = E_b - \Delta E \qquad (8)$$

where E_b is the valence state bonding energy of the metal (or the cohesive energy which can be measured as the enthalpy of sublimation to a gaseous atom with the same electronic configuration as in the metal) and ΔE is the difference between the energy of the ground-state electronic configuration realized in the gas phase and the energy of the exited-state configuration realized in the condensed state. Thus we can estimate ΔH_{subl} knowing the values of $\Delta E(d^4s-d^3s^2)$ or $\Delta E(d^3sp-d^3s^2)$, and E_b.

For the lanthanides and actinides it was shown[17,18] that the bonding energy E_b is a smooth function of the atomic number N. E_b for the group 5 elements V, Nb, and Ta can be determined using eq 8. There, $\Delta E = E(d^4s) - E(d^3s^2)$ for V, Nb, and Ta are experimental spectroscopic data,[11] and $\Delta E = E(d^4s) - E(d^3s^2) = 2.0(\pm 0.4)$ eV for Ha was obtained as a result of the present atomic MCDF calculations. Thus knowing ΔE values for all the elements under consideration and ΔH_{subl}[19] for V, Nb, and Ta, we have found their E_b values. In accordance with the idea developed in ref 18 we see that E_b is a linear function of N for the group 5 elements (Figure 1). Thus we can find E_b for Ha, which together with the value of $\Delta E(d^4s-d^3s^2)$ gives $\Delta H_{subl} = 10.1$ eV or 973.54 kJ/mol. Using $\Delta E(d^3sp-d^3s^2)$ equal to $1.9(\pm 0.4)$ V gives ΔH_{subl}

= 10.2 eV. These estimated values nevertheless seem to be enhanced. Calculations of the sublimation enthalpy at the mixed $d^{4-x}sp^x$ configuration is needed to give the final value of ΔH_{subl} for Ha.

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