Estimation of the gas phase formation enthalpies for superheavy-elements (112, 113, 114, 117, 118, 119 and 120) and some of their +1 and -1 ions

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Abstract In the present work, the gaseous phase formation enthalpies for the elements (and their +1 cations) from groups 1,2, 12, 13, 16, 17 and 18 of the periodic table taken from literature [2,3], the electron integrated heat capacity [4], as well as previously calculated IE and EA [5] are employed to estimate the gas phase formation enthalpies for the superheavy-elements 112 (Copernicium, Cn), 113 (Nionium, Nh), 114 (Flerovium, Fl), 117 (Tennessine, Ts), 118 (Oganesson, Og), 119 and 120 and for some of their +1 and -1 ions. The obtained formation enthalpies ($kJmol^{-1}$) for the elements are: 112 (17.955); 113 (110.360), 114 (70.716); 117 (80.138); 118 (0); 119 (53.688) and 120 (180.400).

Keywords Superheavy-elements; Formation enthalpy; Electron formation enthalpy

Introduction

As has been shown for tennessine [1] despite their simplicity (or may be, because it) extrapolation, combined with some empirical equations, can be a powerful and trustable way to estimate the physical properties of a superheavy-element.

In the present work, literature data [2,3], that is, the gaseous phase formation enthalpies for the elements (and their +1 cations) from groups 1,2, 12, 13, 16, 17 and 18 of the periodic table, the electron integrated heat capacity [4], as well as previously calculated IE and EA [5] are employed to estimate the gas phase formation enthalpies for the superheavy-elements 112 (Copernicium, Cn), 113 (Nionium, Nh), 114 (Flerovium, Fl), 117 (Tennessine, Ts), 118 (Oganesson, Og), 119 and 120 and for some of their +1 and -1 ions.

Methodology, Results and Discussion

In a first moment, the gas phase ΔH_f^θ for the elements and their respective +1 cations were obtained only by extrapolation of literature [2,3] data. In all cases, ΔH_f^θ and $\Delta H_{f(+1)}^\theta$ were plotted as a function of the atomic number (Z). Since for the heavy and superheavy elements, relativistic effects matters [6], in each curve the first element of the group was excluded (except for group 12), in order to obtain a better correlation coefficient. Linear curves, with correlation coefficients from 0.983 to 0.999 were obtained. From the obtained linear equations, the ΔH_f^θ and $\Delta H_{f(+1)}^\theta$ for the superheavy-elements were estimated.

As a secondary approach, the $\Delta H_{f(+1)}^\theta$ values were estimated by using the previously calculated (by scalar relativistic spin-free Hartree-Fock method) first ionizations energies for the superheavy-elements [5], the electron integrated heat capacity (H_T-H_0; named here as $\Delta_f H_{(e-)}^\theta$) was taken as $6.1973 kJmol^{-1}$ [4] and the estimated (by extrapolation) ΔH_f^θ for the neutral elements: $\Delta H_{f(+)}^\theta = IE - \Delta_f H_{(e-)}^\theta + \Delta H_{f(neutral\ ement)}^\theta$. All obtained results are summarized in Table 1.

Table 1: Gas phase formation enthalpies for superheavy-elements and some of their +1 and -1 ions

Elemet/+1 or -1 ion	ΔH_f^θ/kJmol^{-1}	$\Delta H_f^\theta{}_{(+)}$/kJmol^{-1}	$\Delta H_f^\theta{}_{(-)}$/kJmol^{-1}
Cn	17.955[a]		
Cn$^+$		1163.158[a]	
		1132[b]	
Nh	110.360[a]		
Nh$^+$		715.480[a]	
Nh$^-$			171.436[b]
Fl	70.716[a]		
Fl$^+$		739.992[a]	
		617[b]	
Ts	80.138[a]		
Ts$^+$		665.710[a]	
Ts$^-$			-115.928[b]
Og	0[c]		
Og$^+$		781.896[a]	
		978[b]	
119	53.688[a]		
119$^+$		359.185[a]	
119$^-$			53.683[b]
120	180.400[a]		
120$^+$		660.140[a]	
		660[b]	

[a]Obtained by extrapolation of literature [2,3] data. [b]Obtained by using the previously calculated (by scalar relativistic spin-free Hartree-Fock method) first ionizations energies or the first electron affinities for the superheavy-elements [5], the formation enthalpy of the electron, $\Delta_f H^\theta(e^-)$= -6.18 kJmol^{-1} [4] and the estimated (by extrapolation) ΔH_f^θ for the neutral elements. [c]Since it is a noble gas, existing in its most stale form at standard conditions as a monoatomic specie, its formation enthalpy, as of any other noble gas, is zero.

As can be verified, the two approach employed to estimate the $\Delta H_f^\theta{}_{(+)}$values provides results in good agreement, specially for Cn$^+$ and 120$^+$.

For some elements (113, 117 and 119), for which the electron affinities were previously calculated (by scalar relativistic spin-free Hartree-Fock method) [5], the formation enthalpy for the anions $\Delta H_f^\theta{}_{(-)}$were calculated by using the equation: $\Delta H_f^\theta{}_{(-)} = EA + \Delta_f H^\theta{}_{(e-)} + \Delta H_f^\theta{}_{(neutral\ ement)}$. The results are also summarized in Table 1.

When the formation enthalpies are plotted as a function of the calculated Mullikan charges (relativistic Dirac, HF level) a straight line, with r = 0.999 is obtained for the elements 113, 117, 118 and 119, as shown in Figure 1.

When the formation enthalpies are plotted as a function of the calculated Mullikan charges (scalar relativistic spin-free Hartree-Fock method) for all considered elements, the curve shown in Figure 2 is obtained, in which a periodic trend linking both parameters can be verified.

A clear periodic trend can also be observed when the estimated $\Delta H_f^\theta{}_{(+)}$ values are plotted as a function of the atomic number, as shown in Figure 3.
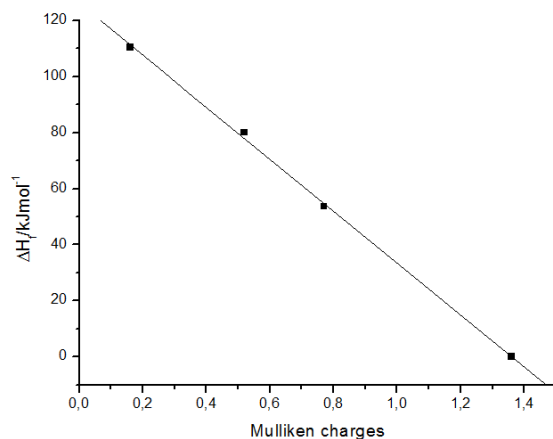
Figure 1: Gas phase formation enthalpy as a Mullikan charge (relativistic Dirac, HF level)[5] function for elements 113, 117, 118 and 119.
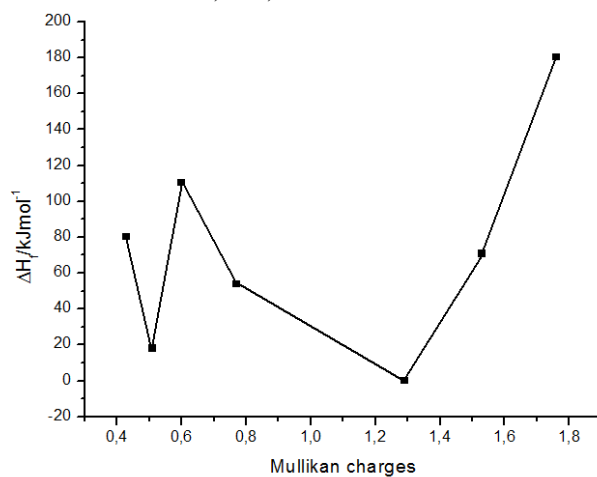

Figure 2: Gas phase formation enthalpies as a function of Mullikan charges (scalar relativistic spin-free Hartree-Fock method) [5] for all considered elements
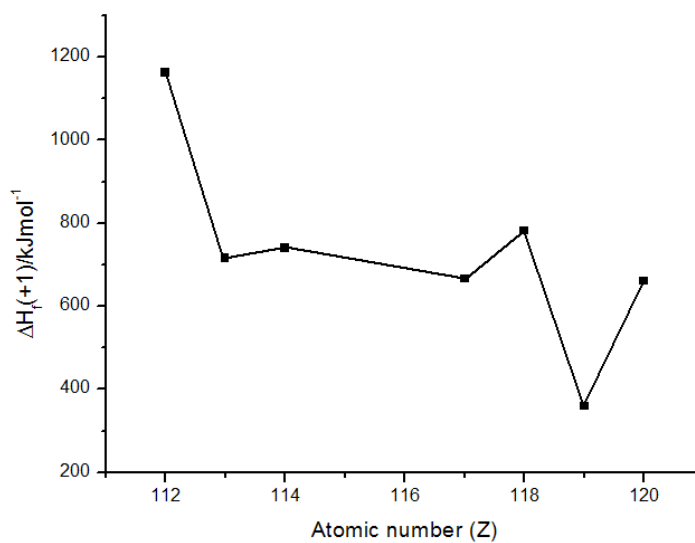
Figure 3: $\Delta H^{\theta}_{f\,(+)}$ values as a function of the atomic number (Z) , for all considered elements

References
1. R.F. de Farias, Chem. Phys. Lett., 667 (2017) 1-3.
2. D.D. Wagman, W.H. Evans; V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey; K.L. Churney; R.L. Nuttall, The NBS tables of chemical thermodynamic properties. *J. Chem. Ref. Data*, , 11 (1982)(supplement nº 2).
3. CRC Handbook of Chemistry and Physics 96th ed., Taylor and Francis, Boca Raton, 2016.
4. J.E. Bartmess, J. Phys. Chem., 98 (1994) 6420-6224.
5. C. Thierfelder, T. Schwerdtfeger, A. Koers, A. Borchevsky, B. Fricke, Phys. Rev. A 80, 022501 2009.
6. B.A. Hess, Relativistic effects in heavy-element chemistry and physics, Wiley, Chichester, 2003.