

# Thermochemistry of Heteroatomic Compounds: analysis and calculation of thermodynamic functions of organometallic compounds of I-IV groups of Mendeleev's Periodic table

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**Abstract:** It is necessary to note, that the heat of vaporization, all thermodynamic functions  $\Delta_{c,i}G^\circ$ ,  $\Delta_{c,i}H^\circ$ ,  $S_0$ ,  $\Delta_c S^\circ_{\text{cond}}$  and heat capacity ( $C_p$ ) of organometallic compounds of I-IV groups of Mendeleev's Periodic Table can be well characterized with the number of valence electrons  $N$  of them. It is difficult to do some conclusions relatively stoichiometric coefficients  $i$  and  $f$  in modified by us Kharasch equation  $\Delta_{\text{vap,c,f,s}}\Psi^\circ = i \pm f * N$  as they concern to organometallic compounds of the different groups. Such conclusion can be made on settlement data of I and II groups only in our opinion. Nevertheless, 43 equations of this type have been created for the processes of vaporization, combustion, formation, entropic transformations and heat capacity. Probably, that such data will help with forecasting of thermochemical functions and parameters of yet not investigated organometallic compounds.

**Keywords:** Organometallic Compounds, Free Energy of Combustion, Free Energy of Formation, Entropy, Heat Capacity, Heat of Combustion Heat of Formation

## 1. Introduction

We have shown earlier [1,2], that the changes of thermodynamic functions  $\Psi^\circ$  ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $C_p$ ), describing processes of vaporization (vap), combustion (c), formation (f), transfer of the heat from a hot body to cold body (entropy, s) and heat capacity various organic and biochemical compounds ( $C_p$ ), can be effectively calculated on the equation (1), which is similarly to known Kharasch equation [3]. In equation (1)  $i$  and  $f$  are stoichiometric coefficients,  $N$  is a number of valence electrons in the researching molecules, from which the number  $h$  of lone electron pairs ( $g=2$ ) of heteroatoms is subtracted or increased [4, 5]

$$\Delta_{\text{vap,c,f,s}}\Psi^\circ = i + f*(N \pm hg) \quad (1)$$

Necessary to add, that in accordance to Kharasch conception "The electronic conception of valence and heats of combustion of organic compounds" [3] the lone electron pairs should not take part in combustion process, apparently. We have chosen the IV<sup>th</sup> group of Periodic Table

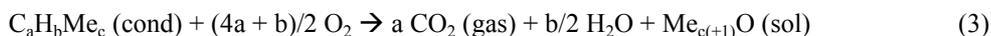
(compounds of carbon and below) as a base point since in these compounds are not present a lone electron pairs ( $hg = 0$ ). According to this position the parameter  $h$  is equal -1 and  $hg = -2$ , для compounds of V<sup>th</sup> group the parameter  $h$  is equal -2 and  $hg = -4$  for VI<sup>th</sup> group and the parameter  $h$  is equal -3 and  $hg = -6$  for VII<sup>th</sup> group of Periodic system. Previously we informed [4], that for organic compounds of I-III groups, having a vacant s- and p-orbitals, necessary to add one, two and three lone electron pairs [4].

But after the careful analysis of valence conditions of metallic atoms of first three groups of Periodic system, we believe that it is not necessary to change of valence of metal (Me) in organometallic compounds of I-IV groups and it is not necessary to add of lone electron pairs on vacant s-and p-orbitals. Therefore the equation (2) represents a new, modified form of the equation (1) which has been used by us for calculations of thermodynamic functions organometallic compounds of I-IV groups of Mendeleev's Periodic Table.

$$\Delta_{\text{vap,c,f,s}}\Psi^\circ = i \pm f * N \quad (2)$$

## 2. Results and Discussion

### 2.1. Organic Compounds of I-II Groups (Lithium, zinc, Cadmium, Mercury)



here Me are Li, Zn, Cd and Hg; a, b, c are stoichiometric coefficients. Necessary thermodynamic data for metal oxides are taken from monograph [28].

Necessary to note that the heat of combustion is more measured and studied than other thermodynamic functions and heat capacity [5].

$$\Delta_c H^\circ = (-249.6 \pm 28.8) - (106.9 \pm 1.4) N r 0.999, S_o 11.9, n 3 \text{ (compounds I-III)} \quad (4)$$

$$\Delta_f H^\circ_{\text{cond}} = (-1053.1 \pm 87.9) + (36.8 \pm 3.2) N r 0.999, S_o 11.3, n 4 \text{ (compounds III-VI)} \quad (5)$$

#### 2.1.2. Zinc Compounds

For Zn-organic compounds it is possible to present the Eqs. (6-9) from which the first characterizes the heats of vaporization. For (VII and VIII) compounds of this group the values of entropy and the heat of capacity in condensed

$$\Delta_{\text{vap}} H^\circ = (19.7 \pm 2.1) + (0.7 \pm 0.05) N r 0.993, S_o 1.5, n 4 \text{ (compounds VII-X)} \quad (6)$$

$$\Delta_c H^\circ = (-286.5 \pm 29.5) - (109.3 \pm 0.8) N r 0.999, S_o 21.6, n 4 \text{ (compounds VII-X)} \quad (7)$$

$$\Delta_f H^\circ_{\text{cond}} = (102.7 \pm 28.9) - (3.9 \pm 0.8) N r 0.961, S_o 21.2, n 4 \text{ (compounds VII-X)} \quad (8)$$

$$\Delta_f H^\circ_{\text{gas}} = (122.1 \pm 31.8) - (3.3 \pm 0.9) N r 0.937, S_o 23.4, n 4 \text{ (compounds VII-X)} \quad (9)$$

The processes of combustion of all these types of organometallic compounds in condensed phase of I-II groups (I-XXII, Table 1) may be presented by the general equation (3) [5]

#### 2.1.1. Lithium Compounds

For the some lithium-organic of compounds (I-VI) are known the heats of vaporization, combustion and formation in condensed and gaseous phases only [6-9]. However these functions can be characterized only by two Eqs. (4 and 5), they are presented in the Table 2 also

state (Table 1) are known. This circumstance enables to calculate the values of combustion entropy ( $\Delta_c S^\circ$ ) on the Hess law (Eq. 10) and then calculate the free energy of combustion and formation ( $\Delta_{c,f} G^\circ$ ) on the Gibbs's Eqs. (11 and 12). All calculated values are summed in Table 1.

Table 1. Thermodynamic functions ( $kJ mol^{-1}$ ,  $J mol^{-1} K^{-1}$ ) of organometallic compounds at P 101 kPa and 298.15 K; all compounds are in condensed state

No comp.	Title of Compound, formula, N	Free energy		Enthalpy (heat contributions)				Entropy and heat capacity		
		$-\Delta_c G^\circ$ (Calc. $\pm 0.5$ ) <sup>a</sup>	$-\Delta_f G^\circ$ (Calc. $\pm 0.5$ ) <sup>b</sup>	$-\Delta_{\text{vap}} H^\circ$	$-\Delta_c H^\circ$	$-\Delta_f H^\circ$	$-\Delta_f H^\circ_{\text{gas}}$	$S^\circ$	$-\Delta_c S^\circ$ (Calc. $\pm 0.5$ ) <sup>f</sup>	$C_p$
1	2	3	4	5	6	7	8	9	10	11
Lithium compounds										
I	Ethyllithium, C <sub>2</sub> H <sub>5</sub> Li, 14			116.6 <sup>[6]</sup> $\pm 0.8$	1741.8 <sup>[6]</sup> $\pm 5.4$		-63.7 <sup>[8]</sup> $\pm 2.2$			
II	2-Methylethyllithium, C <sub>3</sub> H <sub>7</sub> Li, 20				2398.0 <sup>[7]</sup>					
III	Buthyllithium, C <sub>4</sub> H <sub>9</sub> Li, 26			107.1 <sup>[6]</sup> $\pm 2.9$	3025.0 <sup>[6]</sup> $\pm 7.1$	109.5 <sup>[8]</sup> $\pm 3.2$	2.4 <sup>[8]</sup> $\pm 4.3$			
IV	2-Methylpropyllithium, C <sub>4</sub> H <sub>9</sub> Li, 26					88.2 <sup>[7]</sup> $\pm 3.2$				
V	2,2-Dimethylethyllithium, C <sub>4</sub> H <sub>9</sub> Li, 26					92.5 <sup>[7]</sup> $\pm 2.4$				
VI	Phenyllithium, C <sub>6</sub> H <sub>5</sub> Li, 30					-50.4 <sup>[7]</sup> $\pm 2.1$				
Zinc compounds										
VII	Dimethylzinc, C <sub>2</sub> H <sub>6</sub> Zn, 16	1918.4 $\pm 9.6$	85.1 $\pm 0.4$	29.5 <sup>[5]</sup> $\pm 0.4$	2020.0 <sup>[5]</sup> $\pm 5.9$	-25.0 <sup>[8]</sup> $\pm 5.9$	-52.9 <sup>[8]</sup> $\pm 1.3$	201.6 <sup>[9]</sup>	340.6 $\pm 1.7$	129.2 <sup>[9]</sup>
VIII	Diethylzinc, C <sub>4</sub> H <sub>10</sub> Zn, 28	3251.6 $\pm 16.2$	104.5 $\pm 0.5$	40.2 <sup>[5]</sup> $\pm 2.1$	3372.3 <sup>[5]</sup> $\pm 2.1$	-18.0 <sup>c</sup> $\pm 6.0$	-57.0 <sup>c</sup> $\pm 6.0$	290.2 <sup>[10]</sup>	404.7 $\pm 2.0$	194.4 <sup>[10]</sup>
IX	Dipropylzinc, C <sub>6</sub> H <sub>14</sub> Zn, 40			45.6 <sup>[5]</sup> $\pm 2.5$	4653.0 <sup>[5]</sup> $\pm 23.0$	59.0 <sup>[8]</sup> $\pm 23.0$	17.0 <sup>[8]</sup> $\pm 23.0$			
X	Dibutylzinc, C <sub>8</sub> H <sub>18</sub> Zn, 52			54.4 <sup>[5]</sup>	5965.0	106.0	55.0 <sup>[8]</sup>			

No comp.	Title of Compound, formula, <i>N</i>	Free energy		Enthalpy (heat contributions)				Entropy and heat capacity		
		$-\Delta_c G^\circ$ (Calc. $\pm 0.5$ ) <sup>a</sup>	$-\Delta_f G^\circ$ (Calc. $\pm 0.5$ ) <sup>b</sup>	$-\Delta_{\text{vap}} H^\circ$	$-\Delta_c H^\circ$	$-\Delta_f H^\circ$	$-\Delta_f H^\circ_{\text{gas}}$	$S^\circ$	$-\Delta_c S^\circ$ (Calc. $\pm 0.5$ ) <sup>f</sup>	$C_p$
1	2	3	4	5	6	7	8	9	10	11
				$\pm 3.3$	<sup>[5]</sup> $\pm 23.0$	<sup>[8]</sup> $\pm 23.0$	$\pm 23.0$			
Cadmium compounds										
XI	Dimethylcadmium, C <sub>2</sub> H <sub>6</sub> Cd, 16	1890.7 $\pm 9.4$	127.9 $\pm 1.6$	37.1 <sup>d</sup> $\pm 0.1$	1988.0 <sup>[5]</sup> $\pm 12.0$	67.7 <sup>[8]</sup> $\pm 1.3$	104.8 <sup>[8]</sup> $\pm 1.3$	201.88 <sup>e</sup>	329.6 $\pm 1.6$	132.01 <sup>e</sup>
XII	Diethylcadmium, C <sub>4</sub> H <sub>10</sub> Cd, 28			46.0 <sup>[5]</sup> $\pm 1.9$	3349.7 <sup>[5]</sup> $\pm 3.3$	59.3 <sup>[8]</sup> $\pm 1.9$	105.3 <sup>[8]</sup> $\pm 1.9$			
XIII	Dipropylcadmium, C <sub>6</sub> H <sub>14</sub> Cd, 40			54.2 <sup>[27]</sup> $\pm 0.4$	4710.8 <sup>[4]</sup> $\pm 23.5$					
XIV	Dibutylcadmium, C <sub>8</sub> H <sub>18</sub> Cd, 52			67.7 <sup>[27]</sup> $\pm 1.2$						
Mercury compounds										
XV	Dimethylmercury, C <sub>2</sub> H <sub>6</sub> Hg, 16			34.6 <sup>[5]</sup> $\pm 0.8$	1806.7 <sup>[5]</sup>	-57.8 <sup>[8]</sup> $\pm 3.0$	-92.4 <sup>[8]</sup> $\pm 3.1$			
XVI	Diethylmercury, C <sub>4</sub> H <sub>10</sub> Hg, 28			44.8 <sup>[5]</sup> $\pm 1.7$	3103.3 <sup>[5]</sup> $\pm 4.2$	-30.2 <sup>[8]</sup> $\pm 1.5$	90.0 <sup>c</sup> $\pm 0.5$			182.3 <sup>[11]</sup>
XVII	Dipropylmercury, C <sub>6</sub> H <sub>14</sub> Hg, 40			55.2 <sup>[5]</sup> $\pm 1.3$	4341.3 <sup>[5]</sup> $\pm 4.2$	24.9 <sup>[8]</sup> $\pm 5.0$	-30.3 <sup>[8]</sup> $\pm 5.2$			
XVIII	Di-(2-methylethyl)mercury, C <sub>6</sub> H <sub>14</sub> Hg, 40			53.6 <sup>[5]</sup> $\pm 1.7$	4399.5 <sup>[5]</sup> $\pm 4.2$	16.7 <sup>[8]</sup> $\pm 6.0$	-91.2 <sup>[8]</sup> $\pm 4.6$			
XIX	Dibutylmercury, C <sub>8</sub> H <sub>18</sub> Hg, 52			65.3 <sup>[5]</sup> $\pm 4.2$	5622.9 <sup>[5]</sup> $\pm 6.3$	97.7 <sup>[8]</sup> $\pm 6.4$	32.4 <sup>[8]</sup> $\pm 7.7$			
XX	Di-(2-methylpropyl)mercury, C <sub>8</sub> H <sub>18</sub> Hg, 52			63.6 <sup>[5]</sup> $\pm 4.2$	5622.9 <sup>[5]</sup> $\pm 6.3$	101.9 <sup>[8]</sup> $\pm 6.4$	38.3 <sup>[8]</sup> $\pm 7.7$			
XXI	Di-(2-methylbutyl)mercury, C <sub>10</sub> H <sub>21</sub> Hg, 64			71.1 <sup>[5]</sup> $\pm 6.3$	6925.4 <sup>[5]</sup> $\pm 8.4$	153.8 <sup>[8]</sup> $\pm 8.5$	83.0 <sup>[8]</sup> $\pm 11.0$			
XXII	Diphenylmercury, C <sub>12</sub> H <sub>10</sub> Hg, 60			112.8 <sup>[5]</sup> $\pm 0.8$	6431.2 <sup>[5]</sup> $\pm 7.5$	300.0 <sup>c</sup> $\pm 8.0$	410.0 <sup>c</sup> $\pm 8.0$			225.5 <sup>[12]</sup>
Bor compounds										
XXIII	Trimethylborane, C <sub>3</sub> H <sub>6</sub> B, 24			20.2 <sup>[5]</sup> $\pm 0.1$	2989.5 <sup>[5]</sup> $\pm 22.6$	142.7 <sup>[5]</sup> $\pm 22.7$	122.6 <sup>[5]</sup> $\pm 22.7$			
XXIV	Triethylborane, C <sub>6</sub> H <sub>15</sub> B, 42	4861.3 $\pm 24.3$	287.5 $\pm 1.4$	36.8 <sup>[5]</sup> $\pm 0.4$	4975.6 <sup>[5]</sup> $\pm 15.1$	189.1 <sup>[5]</sup> $\pm 5.0$	152.3 <sup>[5]</sup> $\pm 5.0$	330.05 <sup>[13]</sup>	383.8 $\pm 1.9$	240.0 <sup>[13]</sup>
XXV	Tripopylborane, C <sub>9</sub> H <sub>21</sub> B, 60			41.8 <sup>[5]</sup> $\pm 1.2$	6901.1 <sup>[5]</sup> $\pm 13.0$	277.8 <sup>[5]</sup> $\pm 13.8$	236.0 <sup>[5]</sup> $\pm 13.8$			
XXVI	Tributylborane, C <sub>12</sub> H <sub>27</sub> B, 78			61.9 <sup>[5]</sup> $\pm 2.1$	8893.5 <sup>[5]</sup> $\pm 2.1$	352.7 <sup>[5]</sup> $\pm 2.9$	290.8 <sup>[5]</sup> $\pm 3.8$			
XXVII	Tris-(2-methylpropyl)borane, C <sub>12</sub> H <sub>27</sub> B, 78			59.8 <sup>[5]</sup> $\pm 2.1$	8833.7 <sup>[5]</sup> $\pm 5.4$	383.2 <sup>[5]</sup> $\pm 6.3$	323.4 <sup>[5]</sup> $\pm 6.7$			
XXVIII	Tris-(3-methylpropyl)borane, C <sub>12</sub> H <sub>27</sub> B, 78			60.7 <sup>[5]</sup> $\pm 2.1$	8811.9 <sup>[5]</sup> $\pm 25.1$	305.4 <sup>[5]</sup> $\pm 25.1$	242.7 <sup>[5]</sup> $\pm 25.1$			
XXIX	Tris-(2-methylbutyl)borane, C <sub>15</sub> H <sub>33</sub> B, 96			72.0 <sup>[5]</sup> $\pm 2.5$	10801.8 <sup>[5]</sup> $\pm 6.7$	453.1 <sup>[5]</sup> $\pm 7.9$	381.2 <sup>[5]</sup> $\pm 8.4$			
Aluminum compounds										
XXX	Trimethylaluminum, C <sub>3</sub> H <sub>9</sub> Al, 24	2911.6 $\pm 14.5$	182.6 $\pm 0.9$	63.2 <sup>[14]</sup> $\pm 1.7$	3184.4 <sup>[5]</sup> $\pm 9.6$	120.2 <sup>[8]</sup> $\pm 9.7$	57.0 <sup>[8]</sup> $\pm 9.7$	209.4 <sup>[14]</sup>		155.6 <sup>[14]</sup>

No comp.	Title of Compound, formula, <i>N</i>	Free energy		Enthalpy (heat contributions)				Entropy and heat capacity		
		$-\Delta_c G^\circ$ (Calc. $\pm 0.5$ ) <sup>a</sup>	$-\Delta_r G^\circ$ (Calc. $\pm 0.5$ ) <sup>b</sup>	$-\Delta_{\text{vap}} H^\circ$	$-\Delta_c H^\circ$	$-\Delta_r H^\circ$	$-\Delta_r H^\circ_{\text{gas}}$	$S^\circ$	$-\Delta_c S^\circ$ (Calc. $\pm 0.5$ ) <sup>f</sup>	$C_p$
1	2	3	4	5	6	7	8	9	10	11
						$\pm 9.6$				
XXXI	Triethylaluminum, C <sub>6</sub> H <sub>15</sub> Al, 42	5088.0 $\pm 6.3$	309.0 $\pm 1.5$	73.2 <sup>[5]</sup> $\pm 2.1$	5125.4 <sup>[5]</sup> $\pm 8.8$	217.2 <sup>[8]</sup>	144.0 <sup>[8]</sup> $\pm 9.1$	308.0 <sup>[15]</sup>	1255.1 $\pm 6.3$	239.0 <sup>[15]</sup>
XXXII	Tripopylaluminum, C <sub>9</sub> H <sub>21</sub> Al, 54	7010.7 $\pm 35.0$	432.6 $\pm 2.2$	42.5 <sup>[5]</sup> $\pm 1.2$	7058.4 <sup>[5]</sup> $\pm 0.4$	322.3 <sup>[8]</sup>	279.8 <sup>[8]</sup> $\pm 1.9$	370.1 <sup>[16]</sup>	1600.1 $\pm 8.0$	340.5 <sup>[16]</sup>
XXXIII	Tributhylaluminum, C <sub>12</sub> H <sub>27</sub> Al, 78				9046.2 <sup>[5]</sup> $\pm 5.4$	372.5 <sup>[8]</sup>				
XXXIV	Tris-(2-methylpropyl)aluminum, C <sub>12</sub> H <sub>27</sub> Al, 78			61.1 <sup>[17]</sup>	9030.3 <sup>[5]</sup> $\pm 7.5$	388.4 <sup>[8]</sup>	327.3 <sup>[8]</sup>			
Germanium compounds										
XXXV	Tetramethylgermanium, C <sub>4</sub> H <sub>12</sub> Ge, 32	3525.1 $\pm 17.6$	223.3 $\pm 1.1$	27.3 <sup>[18]</sup> $\pm 0.4$	3708.9 <sup>[17]</sup> $\pm 6.3$	134.8 <sup>[8]</sup>	107.5 <sup>[8]</sup> $\pm 6.4$	296.8 <sup>[19]</sup>	616.6 $\pm 3.1$	196.9 <sup>[19]</sup>
XXXVI	Tetraethylgermanium, C <sub>8</sub> H <sub>20</sub> Ge, 56	6105.0 $\pm 30.5$	338.4 $\pm 1.7$	45.7 <sup>[21]</sup> $\pm 0.4$	6356.8 <sup>[5]</sup> $\pm 3.2$	210.6 <sup>[8]</sup>	156.8 <sup>[8]</sup> $\pm 4.8$	428.8 <sup>[20]</sup>	843.6 $\pm 3.1$	294.7 <sup>[20]</sup>
XXXVI I	Tetrapropylgermanium, C <sub>12</sub> H <sub>28</sub> Ge, 80			61.5 <sup>[21]</sup> $\pm 4.2$	8972.6 <sup>[5]</sup> $\pm 2.0$	290.1 <sup>[8]</sup>	228.6 <sup>[8]</sup> $\pm 5.3$			
XXXVI II	Tetraphenylgermanium, C <sub>24</sub> H <sub>20</sub> Ge, 120			164.0 <sup>d</sup> $\pm 4.2$	13139.0 <sup>[17]</sup> $\pm 14.0$	-602.0 <sup>[8]</sup>	-438.0 <sup>[8]</sup> $\pm 15.0$			
Stannum compounds										
XXXIX	Tetramethylstannane, C <sub>4</sub> H <sub>12</sub> Sn, 32	3633.0 $\pm 18.2$	142.7 $\pm 0.7$	32.0 <sup>[18]</sup> $\pm 0.8$	3820.0 <sup>c</sup> $\pm 90.0$	50.0 <sup>c</sup> $\pm 80.0$	20.0 <sup>c</sup> $\pm 80.0$	310.8 <sup>[22]</sup>	627.0 $\pm 3.1$	197.9 <sup>[22]</sup>
XL	Tetraethylstannane, C <sub>8</sub> H <sub>20</sub> Sn, 56			50.6 <sup>[18]</sup> $\pm 0.2$	6489.4 <sup>[5]</sup> $\pm 8.4$	92.6 <sup>[8]</sup>	42.0 <sup>[8]</sup> $\pm 2.6$			301.7 <sup>[23]</sup>
XLI	Tetrapropylstannane, C <sub>12</sub> H <sub>28</sub> Sn, 80			65.4 <sup>[18]</sup> $\pm 2.5$	9093.1 <sup>[5]</sup> $\pm 5.0$	208.3 <sup>[8]</sup>	142.9 <sup>[8]</sup> $\pm 5.9$			
XLII	Tetrakis-(1-methylethyl)stannane, C <sub>12</sub> H <sub>28</sub> Sn, 80			64.9 <sup>[17]</sup> $\pm 4.2$	9096.4 <sup>[5]</sup> $\pm 3.8$	184.5 <sup>[8]</sup>	119.6 <sup>[8]</sup> $\pm 7.1$			
XLIII	Tetrabutylstannane, C <sub>16</sub> H <sub>36</sub> Sn, 104			82.8 <sup>b</sup> $\pm 2.1$	11717.3 <sup>[5]</sup> $\pm 6.7$	300.2 <sup>[8]</sup>	217.4 <sup>[8]</sup> $\pm 4.5$			
XLIV	Tetrakis-(1-methylpropyl)stannane, C <sub>16</sub> H <sub>36</sub> Sn, 104				11690.9 <sup>[5]</sup> $\pm 5.9$	327.8 <sup>[8]</sup>				
XLV	Tetraphenylstannane, C <sub>24</sub> H <sub>20</sub> Sn, 120			161.1 <sup>[24]</sup> $\pm 4.2$	13566.6 <sup>[5]</sup> $\pm 7.1$	-412.3 <sup>[5]</sup>	-478.6 <sup>[5]</sup> $\pm 4.0$			426.3 <sup>[12]</sup>
Lead compounds										
XLVI	Tetramethyllead, C <sub>4</sub> H <sub>12</sub> Pb, 32	3529.7 $\pm 17.6$	193.5 $\pm 1.0$	38.0 <sup>[5]</sup> $\pm 0.4$	3711.2 <sup>[25]</sup> $\pm 1.3$	-98.1 <sup>[8]</sup>	-136.1 <sup>[8]</sup> $\pm 4.4$	320.0 <sup>[25]</sup>	608.6 $\pm 3.0$	202.5 <sup>[25]</sup>
XLVII	Tetraethyllead, C <sub>8</sub> H <sub>20</sub> Pb, 56	6375.2 $\pm 31.9$	191.5 $\pm 1.0$	56.6 <sup>[18]</sup> $\pm 1.0$	6383.5 <sup>[25]</sup> $\pm 2.5$	-53.0 <sup>[8]</sup>	-109.6 <sup>[8]</sup> $\pm 5.1$	464.6 <sup>[15]</sup>	27.8 $\pm 0.1$	307.4 <sup>[15]</sup>
XLVIII	Tetrapropyllead, C <sub>12</sub> H <sub>28</sub> Pb, 80				9055.8 <sup>[4]</sup> $\pm 45.3$					
XLIX	Tetraphenyllead, C <sub>24</sub> H <sub>20</sub> Pb, 120			159.0 <sup>[26]</sup> $\pm 1.0$	13036.0 <sup>[17]</sup> $\pm 15.0$	-515.0 <sup>[8]</sup>	-674.0 <sup>[8]</sup> $\pm 15.0$			

<sup>a</sup> Calc. through Eq. (11); <sup>b</sup> Calc. through Eq. (12); <sup>c</sup> Average of 6-7 values; <sup>d</sup> Calculated as a difference between  $\Delta_r H^\circ_{\text{cond}} - \Delta_r H^\circ_{\text{gas}}$ ; <sup>e</sup> Data compiled from <http://webbook.nist.gov/chemistry/>; <sup>f</sup> Calc. through Eq. (10).

$$\Delta_c S_{\text{cond}} = \sum n_i S_{\text{products}} - \sum n_j S_{\text{reactants}} \quad (10)$$

here  $n_i$  and  $n_j$  are stoichiometric coefficients.

$$\Delta_c G^{\circ} = \Delta_c H^{\circ} - 298.15 \cdot \Delta_c S^{\circ} \quad (11)$$

$$\Delta_f G^{\circ} = \Delta_f H^{\circ} - 298.15 \cdot S^{\circ} \quad (12)$$

### 2.1.3. Cadmium Compounds

Thermodynamics with cadmium organic compounds it is

$$\Delta_{\text{vap}} H^{\circ} = (22.9 \pm 2.8) + (0.8 \pm 0.07) N r 0.993, S^{\circ} 1.9, n 4 \text{ (compounds XI-XIV)} \quad (13)$$

$$\Delta_c H^{\circ} = (174.4 \pm 3.6) - (113.4 \pm 0.02) N r 0.999, S^{\circ} 26.7, n 3 \text{ (compounds XI-XIII)} \quad (14)$$

similar to a situation with Zn-compounds. Data on entropy and the heat of capacity in condensed state are known; on this basis the values of free energies of combustion and formation ( $\Delta_{c,r} G^{\circ}$ ) for compound (XI, Table 1) are calculated (Eqs. 11 and 12).

The Eqs. (13 and 14) for heats of vaporization and combustion according to for compounds (XI-XIV) are calculated also (Table 2).

**Table 2.** The parameters of equations  $\Delta \Psi^{(o)} (kJ mol^{-1} \text{ and } J mol^{-1} K^{-1}) = i \pm f * N$  for vaporization, combustion, formation of organometallic compounds;  $P$  101 kPa;  $T$  298.15 K

The functions of processes	No Eq. in text	$i$	$f$	$r$	$S^{\circ}$	Nos. of compounds in Table
	2	3	4	5	6	7
<b>Lithium compounds</b>						
$\Delta_c H^{\circ}$	4	-249.6 ± 28.8	-106.9 ± 1.4	0.999	11.9	I-III
$\Delta_f H^{\circ}_{\text{cond}}$	5	-1053.1 ± 87.9	36.8 ± 3.2	0.999	11.3	III-VI
<b>Zinc compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	6	19.7 ± 2.1	0.7 ± 0.05	0.993	1.5	VII-X
$\Delta_c H^{\circ}$	7	-286.5 ± 29.5	-109.3 ± 0.8	0.999	21.6	VII-X
$\Delta_f H^{\circ}_{\text{cond}}$	8	102.7 ± 28.9	-3.9 ± 0.8	0.961	21.2	VII-X
$\Delta_f H^{\circ}_{\text{gas}}$	9	122.1 ± 28.9	-3.3 ± 0.9	0.937	23.4	VII-X
<b>Cadmium compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	13	22.9 ± 2.8	0.8 ± 0.07	0.993	1.9	XI-XIV
$\Delta_c H^{\circ}$	14	174.4 ± 3.6	-113.4 ± 0.02	0.999	26.7	XI-XIII
<b>Mercury compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	15	22.9 ± 1.4	0.8 ± 0.03	0.995	1.3	XV-XXI
$\Delta_c H^{\circ}$	16	-131.1 ± 31.2	-105.7 ± 0.7	0.999	28.8	XV-XXII
$\Delta_f H^{\circ}_{\text{cond}}$	17	148.8 ± 17.6	-4.7 ± 0.4	0.986	15.4	XV, XVI, XVIII-XXI
$\Delta_f H^{\circ}_{\text{gas}}$	18	191.7 ± 43.7	-4.1 ± 1.0	0.903	38.4	XV, XVI, XVIII-XXI
<b>Bor compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	21	3.5 ± 3.2	0.7 ± 0.05	0.990	2.8	XXIII-XXIX
$\Delta_c H^{\circ}$	22	-405.4 ± 33.6	-108.3 ± 0.5	0.999	29.6	XXIII-XXIX
$\Delta_f H^{\circ}_{\text{cond}}$	23	-24.5 ± 32.9	-4.2 ± 0.5	0.970	28.9	XXIII-XXIX
$\Delta_f H^{\circ}_{\text{gas}}$	24	-21.2 ± 34.7	-3.5 ± 0.5	0.952	30.5	XXIII-XXIX
<b>Aluminum compounds</b>						
$\Delta_c G^{\circ}$	25	412.4 ± 450.1	-135.4 ± 10.7	0.997	229.6	XXX-XXXII
$\Delta_f G^{\circ}_{\text{cond}}$	26	21.1 ± 37.5	-8.2 ± 0.9	0.994	19.1	XXX-XXXII
$\Delta_c H^{\circ}$	27	-720.4 ± 406.9	-108.1 ± 6.9	0.994	322.5	XXX-XXXIV
$\Delta_f H^{\circ}_{\text{cond}}$	28	-23.2 ± 37.2	-4.7 ± 0.6	0.974	29.4	XXX-XXXIV
$\Delta_f H^{\circ}_{\text{gas}}$	29	128.6 ± 74.2	-7.2 ± 1.8	0.971	37.9	XXX-XXXII
$S^{\circ}_{\text{cond}}$	30	81.2 ± 3.5	5.4 ± 0.1	0.999	1.8	XXX-XXXII
$\Delta_c S^{\circ}_{\text{cond}}$	31	-355.7 ± 112.8	-22.5 ± 2.7	0.993	57.5	XXX-XXXII
<b>Germanium compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	33	-32.8 ± 25.8	1.5 ± 0.3	0.953	21.3	XXXV-XXXVIII
$\Delta_c H^{\circ}$	34	-333.2 ± 88.3	-107.1 ± 1.1	0.999	72.2	XXXV-XXXVIII
$\Delta_f H^{\circ}_{\text{cond}}$	35	-30.6 ± 2.6	-3.2 ± 0.05	0.999	1.5	XXXV-XXXVII
<b>Stannum compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	36	10.3 ± 1.4	0.7 ± 0.02	0.998	1.1	XXXIX-XLIII
$\Delta_c H^{\circ}$	37	-299.0 ± 88.3	-110.0 ± 0.5	0.999	40.6	XXXIX-XLV
$\Delta_f H^{\circ}_{\text{cond}}$	38	97.7 ± 32.2	-3.8 ± 0.4	0.979	25.2	XXXIX-XLIV
$\Delta_f H^{\circ}_{\text{gas}}$	39	90.3 ± 31.2	-2.8 ± 0.4	0.969	22.9	XXXIX-XLIII
<b>Lead compounds</b>						
$\Delta_{\text{vap}} H^{\circ}$	40	-14.0 ± 13.9	1.4 ± 0.2	0.992	11.4	XLVI, XLVII, XLIX
$\Delta_c H^{\circ}$	41	-417.2 ± 184.0	-106.0 ± 2.3	0.999	151.4	XLVI-XLIX
$\Delta_f H^{\circ}_{\text{cond}}$	42	-141.9 ± 153.3	5.2 ± 1.9	0.937	125.4	XLVI, XLVII, XLIX
$\Delta_f H^{\circ}_{\text{gas}}$	43	-155.9 ± 167.2	6.7 ± 2.1	0.953	136.8	XLVI, XLVII, XLIX

### 2.1.4. Mercury Compounds

The heat contributions (enthalpies) are known for 8 compounds (XV-XXII, Table 1). These data have allowed to calculate four equations (15-18) for vaporization,

$$\Delta_{\text{vap}}H^{\circ} = (22.9 \pm 1.4) + (0.8 \pm 0.03) Nr 0.995, S_0 1.3, n 7 \text{ (compounds XV-XXI)} \quad (15)$$

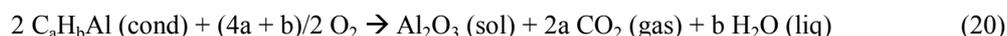
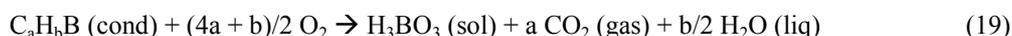
$$\Delta_c H^{\circ} = (-131.1 \pm 31.2) - (105.3 \pm 0.8) Nr 0.999, S_0 28.8, n 8 \text{ (compounds XV-XXII)} \quad (16)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (148.8 \pm 17.6) - (4.7 \pm 0.4) Nr 0.986, S_0 15.4, n 6 \text{ (compounds XV, XVI, XVIII-XXI)} \quad (17)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (191.7 \pm 43.8) - (4.1 \pm 1.0) Nr 0.903, S_0 38.4, n 6 \text{ (compounds XV, XVI, XVIII-XXI)} \quad (18)$$

### 2.2. Organic Compounds of III Group (Bor, Aluminum)

The processes of combustion of these types of organometallic compounds in condensed phase of III group (XXIII-XXXIV, Table 1) may be presented by the different equations. So, the combustion of organoboranes (XXIII-



The thermochemical parameters are known for 7 of boranes (XXIII-XXIX, Table 1). These data have allowed

$$\Delta_{\text{vap}}H^{\circ} = (3.5 \pm 3.2) + (0.7 \pm 0.05) Nr 0.990, S_0 2.8, n 7 \text{ (compounds XXIII-XXIX)} \quad (21)$$

$$\Delta_c H^{\circ} = (-405.4 \pm 33.6) - (108.3 \pm 0.5) Nr 0.999, S_0 29.6, n 7 \text{ (compounds XXIII-XXIX)} \quad (22)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (-24.5 \pm 32.9) - (4.2 \pm 0.5) Nr 0.970, S_0 28.9, n 7 \text{ (compounds XXIII-XXIX)} \quad (23)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (-21.2 \pm 34.7) - (3.5 \pm 0.5) Nr 0.952, S_0 30.5, n 7 \text{ (compounds XXIII-XXIX)} \quad (24)$$

The organic compounds of aluminum (XXX-XXXIV) have appeared more "richer" on thermodynamic data than the previous types of compounds. The heats of vaporization, combustion, formation in condensed and gaseous phases, entropy of formation and heat capacity there are for its (Table 1). Such circumstance has allowed to calculate for

$$\Delta_c G^{\circ} = (412.4 \pm 450.1) - (135.4 \pm 10.7) Nr 0.997, S_0 229.6, n 3 \text{ (compounds XXX-XXXII)} \quad (25)$$

$$\Delta_f G^{\circ}_{\text{cond}} = (21.1 \pm 37.5) - (8.2 \pm 0.9) Nr 0.994, S_0 19.1, n 3 \text{ (compounds XXX-XXXII)} \quad (26)$$

$$\Delta_c H^{\circ} = (-720.4 \pm 406.9) - (108.1 \pm 6.9) Nr 0.994, S_0 322.5, n 5 \text{ (compounds XXX-XXXIV)} \quad (27)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (-23.2 \pm 37.2) - (4.7 \pm 0.6) Nr 0.974, S_0 29.6, n 5 \text{ (compounds XXX-XXXIV)} \quad (28)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (128.6 \pm 74.2) - (7.2 \pm 1.8) Nr 0.971, S_0 37.9, n 3 \text{ (compounds XXX-XXXII)} \quad (29)$$

$$S^{\circ}_{\text{cond}} = (81.2 \pm 3.5) + (5.4 \pm 0.1) Nr 0.999, S_0 1.8, n 3 \text{ (compounds XXX-XXXII)} \quad (30)$$

$$\Delta_c S^{\circ}_{\text{cond}} = (-355.7 \pm 112.8) - (22.5 \pm 2.7) Nr 0.993, S_0 57.5, n 3 \text{ (compounds XXX-XXXII)} \quad (31)$$

### 2.3. Organic Compounds of IV Group (Germanium, Stannum, Lead)

It is necessary to note, that in the given work are not considered carbon organic compounds because of this huge

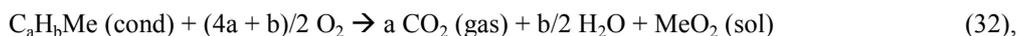
combustion and formation in condensed and gaseous phases

XXIX) conducts to formation of boric acid, carbon dioxide and water (Eq. 19), but at the combustion of organoaluminums (XXX-XXXIV) are formed aluminum oxide, carbon dioxide and water (Eq. 20) [5, 28]

to calculate four equations (21-24) for vaporization, combustion and formation in condensed and gaseous phases

compounds (XXX-XXXII) the entropies of combustion, free energies of combustion and formation (Table 1) via Eqs. (10-12) and receive seven Eqs. (25-31), reflecting the interrelations between the mentioned above thermodynamic functions and a number of valence electrons  $N$  in their molecules

class of compounds the separate paper is devoted [29]. The process of combustion of fourth group of organometallic compounds in condensed phase (XXXV-XLIX, Table 1) may be presented by the general equation (32).



here Me are Ge, Sn, Pb; a and b are stoichiometric coefficients.

### 2.3.1. Germanium Compounds

Entropy of formation ( $S_{\text{cond}}^{\circ}$ ) in condensed state is available for Ge-compounds (XXXV and XXXVI), that

$$\Delta_{\text{vap}}H^{\circ} = (-32.8 \pm 25.8) + (1.5 \pm 0.3) Nr 0.953, S_0 21.3, n 4 \text{ (compounds XXXV-XXXVIII)} \quad (33)$$

$$\Delta_c H^{\circ} = (-333.2 \pm 88.3) - (107.1 \pm 1.1) Nr 0.999, S_0 72.2, n 4 \text{ (compounds XXXV-XXXVIII)} \quad (34)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (-30.6 \pm 2.6) - (3.2 \pm 0.05) Nr 0.999, S_0 1.5, n 3 \text{ (compounds XXXV-XXXVII)} \quad (35)$$

### 2.3.2. Stannum and Lead Compounds

The similar situation has turned out for organic compounds of stannum (XXXIX-XLV) and lead (XLVI-XLIX). For both classes of compounds the equations of

$$\Delta_{\text{vap}}H^{\circ} = (10.3 \pm 1.4) + (0.7 \pm 0.02) Nr 0.998, S_0 1.1, n 5 \text{ (compounds XXXIX-XLIII)} \quad (36)$$

$$\Delta_c H^{\circ} = (-299.0 \pm 88.3) - (110.0 \pm 0.5) Nr 0.999, S_0 40.6, n 7 \text{ (compounds XXXIX-XLV)} \quad (37)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (97.7 \pm 32.2) - (3.8 \pm 0.4) Nr 0.979, S_0 25.2, n 5 \text{ (compounds XXXIX-XLIV)} \quad (38)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (90.3 \pm 31.2) - (2.8 \pm 0.4) Nr 0.969, S_0 22.9, n 5 \text{ (compounds XXXIX-XLIII)} \quad (39)$$

$$\Delta_{\text{vap}}H^{\circ} = (-14.3 \pm 13.9) + (1.4 \pm 0.2) Nr 0.992, S_0 11.4, n 3 \text{ (compounds XLVI, XLVII, XLIX)} \quad (40)$$

$$\Delta_c H^{\circ} = (-417.2 \pm 184.0) - (106.0 \pm 2.3) Nr 0.999, S_0 151.4, n 4 \text{ (compounds XLVI-XLIX)} \quad (41)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (-141.9 \pm 153.3) + (5.2 \pm 1.9) Nr 0.937, S_0 125.4, n 3 \text{ (compounds XLVI, XLVII, XLIX)} \quad (42)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (-155.9 \pm 164.2) + (6.7 \pm 2.1) Nr 0.953, S_0 136.8, n 3 \text{ (compounds XLVI, XLVII, XLIX)} \quad (43)$$

Entropy of formation ( $S_{\text{cond}}^{\circ}$ ) in condensed state is available for Sn-compound (XXXIX) and for Pb-compounds (XLVI and XLVII), that creates an opportunity of calculation of combustion entropy ( $\Delta_c S_{\text{cond}}^{\circ}$ ) and free energies of combustion and formation ( $\Delta_{c,f} G^{\circ}$ ) (Table 1) for them on the equations (10-12) as it has been made for organometallic compounds I-III groups.

## 3. Conclusion

It is necessary to note, that the heat of vaporization, all thermodynamic functions  $\Delta_{c,f} G^{\circ}$ ,  $\Delta_{c,f} H^{\circ}$ ,  $\Delta_c S_{\text{cond}}^{\circ}$  and heat capacity ( $C_p$ ) organometallic compounds of I-IV groups of Mendeleev's Periodic Table can be well characterized with the number of valence electrons  $N$  of them.

It is difficult to do what or the conclusions rather stoichiometric coefficients  $i$  and  $f$  in modified by us Kharasch equation  $\Delta_{\text{vap,c,f,s}} \psi^{\circ} = i \pm f * N$  as they concern to organometallic compounds of the different groups. Such conclusion can be made on settlement data of I and II groups only in our opinion.

It is necessary to note, that coefficients  $i$  and  $f$  in the equations (6, 13, 15) on processes vaporization of zinc, cadmium and mercury compounds are close enough among

creates an opportunity of calculation of combustion entropy ( $\Delta_c S_{\text{cond}}^{\circ}$ ) and free energies of combustion and formation ( $\Delta_{c,f} G^{\circ}$ ) (Table 1) for them on the equations (10-12). The known the heats of vaporization, combustion and formation enable to receive Eqs. (33-35)

vaporization, combustion and formation in condensed and gaseous phases processes are calculated: Eqs. (36-39) for Sn-compounds and Eqs. (40-43) for Pb-compounds

themselves (19.7 – 22.9 and 0.7 – 0.8 correspondingly). The coefficients  $i$  in equations (4, 7, 14, 16), describing combustion processes differ among themselves (-131.1 – 174.4) a little, while  $f$  coefficients (-105.7 – -109.3) are similar to known value -109.0 kJ mol<sup>-1</sup> for alkanes [3]. The coefficient  $i$  essentially differs (-1053.1 kJ mol<sup>-1</sup>) for formation in condensed phase only for Li-organic compounds. The same coefficients for Zn, Cd and Hg compounds are close among themselves for formation processes as condensed and gaseous phases.

Probably, that such data will help with forecasting of thermochemical functions and parameters of yet not investigated organometallic compounds.

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