

Thermochemistry of heteroatomic compounds: analysis and calculation of thermodynamic functions of organic compounds of V-VII groups of Mendeleev's Periodic table

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Abstract: The heat of vaporization ($\Delta_{\text{vap}}H^\circ$), all thermodynamic functions $\Delta_{\text{c,r}}G^\circ$, $\Delta_{\text{c,r}}H^\circ$, S° , $\Delta_{\text{c}}S^\circ_{\text{cond}}$ and heat capacity (C_p) of organic compounds of V-VII groups of Mendeleev's Periodic Table can be well characterized with the number of valence electrons N without taking into account the number (h) of lone electrons pairs (g) of them in equation $\Delta_{\text{vap,c,r,s}}\Psi^\circ = i \pm f^*(N - hg)$. The stoichiometric coefficients i and f reflect partially a various spatial structure of all investigated compounds. The free energy and entropy of combustion and formation are calculated only for oxygen, sulfur and partly fluorine compounds. For this reason their analysis causes the certain difficulties. It is possible to note, that f coefficients in the given above equation for free energies of combustion are very close to such coefficients for the heat of combustion processes. Also it has been found that calculated thermodynamic functions of ethers and sulfides are in good interdependence from each other: $\Delta_{\text{c}}H^\circ - \Delta_{\text{c}}S^\circ_{\text{cond}}$, $\Delta_{\text{f}}H^\circ - S^\circ_{\text{cond}}$, $S^\circ_{\text{cond}} - C_p$. The 74 equations of mentioned type have been created for processes of vaporization, combustion, formation, entropic transformations and heat capacity.

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

1. Introduction

In the present communication we continue to analyze and calculate the changes of thermodynamic functions $\Delta\Psi^\circ$ (ΔG° , ΔH° , ΔS°), characterizing the processes of vaporization, combustion and formation of the condensed and gaseous organic compounds and their heat capacities (C_p) of V-VII groups of Mendeleev's Periodic Table.

Previously we have repeatedly shown, that not only the heat of combustion of organometallic compounds of I-IV groups of Periodic Table [1], organic [2, 3] and biochemical compounds, such as different carbohydrates [4] and amino acids [5] in the dependence from the number of their valence electrons N are.

We hope to investigate same interrelations (Equation 1, in which i and f are stoichiometric coefficients) in the rows of mentioned above of heteroatomic compounds now

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

We wished to remind, that in accordance to Kharasch

conception "The electronic conception of valence and heats of combustion of organic compounds" [6] the number (h) of lone electron pairs ($g = 2$) should not take part in the combustion process, apparently. We have chosen the IVth group of Periodic Table (compounds of carbon and below) as a base point since in these compounds are not present a lone electron pairs ($hg = 0$) [7]. According to this position the parameter h is equal to 1 and $hg = 2$, for compounds of Vth group the parameter h is equal to 2 and $hg = 4$ for VIth group and the parameter h is equal to 3 and $hg = 6$ for VIIth group of Periodic system [7].

2. Results and Discussion

2.1. Organic Compounds of Vth Group (Trialkyl (Aryl)Amines and -Phosphines)

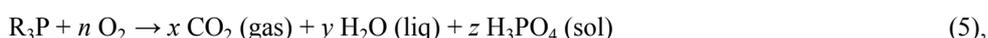
The analysis of thermodynamic functions of nitrogen (I-IX) and phosphorus (X-XIV, Table 1) compounds should be begun with consideration of their heats of vaporization ($\Delta_{\text{vap}}H^\circ$). This thermochemical parameter quantitatively

depends from a number of valence electrons N , from which is subtracted one (h) lone electron pair, hence contribution hg is equally 2 (Eqs. 2 and 3, they are presented in Table 2 also)

$$\Delta_{\text{vap}}H^{\circ} = (8.3 \pm 10.4) + (0.7 \pm 0.1)(N - hg) \quad r \ 0.960, S_0 \ 11.2, n \ 5 \text{ (compounds I-III, VI, IX)} \quad (2)$$

$$\Delta_{\text{vap}}H^{\circ} = (-8.4 \pm 1.4) + (1.4 \pm 0.2)(N - hg) \quad r \ 0.991, S_0 \ 9.1, n \ 3 \text{ (compounds X-XII)} \quad (3)$$

Processes of combustion of the same nitrogen and phosphorus organic compounds can be presented by the following schemes (4 and 5)



in which n, x, y, z are stoichiometric coefficients, and R are Alkyl, Aryl. of heteroatomic compounds (Table 1) allow to produce the following Eqs. (6 and 7).

The analysis of the combustion heats of these two groups

$$\Delta_c H^{\circ} = (-21.8 \pm 29.5) - (108.8 \pm 0.4)(N - hg) \quad r \ 0.999, S_0 \ 39.5, n \ 9 \text{ (compounds I-IX)} \quad (6)$$

$$\Delta_c H^{\circ} = (-854.8 \pm 45.4) - (107.0 \pm 0.5)(N - hg) \quad r \ 0.999, S_0 \ 52.8, n \ 5 \text{ (compounds X-XIV)} \quad (7)$$

It is necessary to note, that stoichiometric coefficients f in these equations are very close to coefficient $-109.0 \text{ kJ mol}^{-1} \text{ electron}^{-1}$ for the similar equations on combustion of alkanes [3], nitro compounds [2], carbohydrates [4] and amino acids [5]. The heats of formation of nitrogen and phosphorus compounds in condensed and gas phases are characterized by good dependences (8-11, Table 2) also.

$$\Delta_f H^{\circ}_{\text{cond}} = (52.8 \pm 23.9) - (4.3 \pm 0.2)(N - hg) \quad r \ 0.991, S_0 \ 21.2, n \ 9 \text{ (compounds I-IX)} \quad (8)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (50.4 \pm 4.0) - (3.5 \pm 0.04)(N - hg) \quad r \ 0.999, S_0 \ 4.2, n \ 4 \text{ (compounds I-III, VI)} \quad (9)$$

$$\Delta_f H^{\circ}_{\text{cond}} = (-191.5 \pm 58.2) + (3.9 \pm 0.6)(N - hg) \quad r \ 0.964, S_0 \ 67.7, n \ 5 \text{ (compounds X-XIV)} \quad (10)$$

$$\Delta_f H^{\circ}_{\text{gas}} = (-284.3 \pm 4.0) + (7.1 \pm 1.2)(N - hg) \quad r \ 0.985, S_0 \ 60.4, n \ 3 \text{ (compounds X-XII)} \quad (11)$$

The values entropy of formation and heat capacity are known for compounds (I and VI, Table 1) only. Nevertheless the first of them has allowed to calculate the entropy of combustion for trimethylamine (I) into the accordance with the scheme (4) and equation (12). The required values of entropy of formation for molecules CO_2 , H_2O and N_2 (213.8, 70.1 and 191.5 $\text{J mol}^{-1} \text{ K}^{-1}$ correspondingly) were taken in monograph [8].

$$\Delta_c S^{\circ}_{\text{cond}} = \sum n_i S^{\circ}_{\text{products}} - \sum n_j S^{\circ}_{\text{reactants}} \quad \text{here } n_i \text{ and } n_j \text{ are stoichiometric coefficients} \quad (12)$$

In turn, the value of $\Delta_c S^{\circ}_{\text{cond}}$ has enabled to calculate the energies of combustion and formation (Table 1) in condensed state for amine (I) through the Eqs. (13 and 14)

$$\Delta_c G^{\circ} = \Delta_c H^{\circ} - 298.15 \cdot \Delta_c S^{\circ} \quad (13)$$

$$\Delta_f G^{\circ} = \Delta_f H^{\circ} - 298.15 \cdot S^{\circ} \quad (14)$$

2.2. Organic Compounds of V^{th} Group

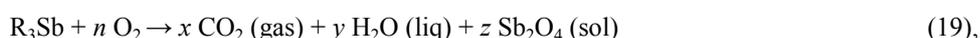
x(Trialkyl(Aryl)Arsines, -Stibines and -Bismuthines)

$$\Delta_{\text{vap}}H^{\circ} = (-9.0 \pm 10.8) + (1.5 \pm 0.2)(N - hg) \quad r \ 0.992, S_0 \ 9.2, n \ 3 \text{ (compounds XV-XVII)} \quad (15)$$

$$\Delta_{\text{vap}}H^{\circ} = (1.9 \pm 7.8) + (1.2 \pm 0.1)(N - hg) \quad r \ 0.993, S_0 \ 6.8, n \ 3 \text{ (compounds XXVIII-XX)} \quad (16)$$

$$\Delta_{\text{vap}}H^{\circ} = (5.3 \pm 9.8) + (1.2 \pm 0.2)(N - hg) \quad r \ 0.990, S_0 \ 2.8, n \ 3 \text{ (compounds XXI-XXIII)} \quad (17)$$

The processes of combustion of arsenic, stibium and bismuth compounds it is possible to present three following schemes (18-20)





in which n, x, y, z are stoichiometric coefficients, and R is Alk, Ar.

The use of literary values ([Reference 9]?) of the heats of combustion and formation in condensed and gas phase for

compounds (XV-XXIII, Table 1) has enabled to calculate the Eqs. (21-23 for arsenic compounds, 24-26 for stibium compounds and 27-29 for bismuth compounds, Table 2)

$$\Delta_c H^0 = (-385.8 \pm 70.7) - (110.3 \pm 1.2) (N - hg) \quad r \ 0.999, S_0 \ 59.6, n \ 3 \ (\text{compounds XV-XVII}) \quad (21)$$

$$\Delta_f H^0_{\text{cond}} = (-198.0 \pm 77.2) + (6.6 \pm 1.3) (N - hg) \quad r \ 0.979, S_0 \ 65.1, n \ 3 \ (\text{compounds XV-XVII}) \quad (22)$$

$$\Delta_f H^0_{\text{gas}} = (-207.9 \pm 87.5) + (8.0 \pm 1.5) (N - hg) \quad r \ 0.982, S_0 \ 73.7, n \ 3 \ (\text{compounds XV-XVII}) \quad (23)$$

$$\Delta_c H^0 = (-528.6 \pm 34.6) - (107.8 \pm 0.6) (N - hg) \quad r \ 0.999, S_0 \ 29.2, n \ 3 \ (\text{compounds XVIII-XX}) \quad (24)$$

$$\Delta_f H^0_{\text{cond}} = (-155.5 \pm 80.0) + (5.3 \pm 1.4) (N - hg) \quad r \ 0.967, S_0 \ 67.1, n \ 3 \ (\text{compounds XVIII-XX}) \quad (25)$$

$$\Delta_f H^0_{\text{gas}} = (-152.6 \pm 88.5) + (6.5 \pm 1.5) (N - hg) \quad r \ 0.973, S_0 \ 74.6, n \ 3 \ (\text{compounds XVIII-XX}) \quad (26)$$

$$\Delta_c H^0 = (-621.4 \pm 113.2) - (106.6 \pm 2.0) (N - hg) \quad r \ 0.999, S_0 \ 95.4, n \ 3 \ (\text{compounds XXI-XXIII}) \quad (27)$$

$$\Delta_f H^0_{\text{cond}} = (14.5 \pm 68.5) + (5.0 \pm 1.2) (N - hg) \quad r \ 0.973, S_0 \ 57.7, n \ 3 \ (\text{compounds XXI-XXIII}) \quad (28)$$

$$\Delta_f H^0_{\text{gas}} = (18.6 \pm 77.3) + (6.2 \pm 1.3) (N - hg) \quad r \ 0.977, S_0 \ 65.2, n \ 3 \ (\text{compounds XXI-XXIII}) \quad (29)$$

The known data (Which?[9]) on heat capacity for arsenic compounds (XV-XVII) have allowed to receive the

equation (30), which reflect the interdependence between the C_p values and the number of valence electrons ($N-hg$)

$$C_p = (117.2 \pm 32.5) + (2.3 \pm 0.6) (N - hg) \quad r \ 0.973, S_0 \ 27.4, n \ 3 \ (\text{compounds XV-XVII}) \quad (30)$$

The entropy and free energies of combustion and formation in condensed state are calculated for

trimethylarsine (XV) only (Table 1).

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

No comp.	Title of Compound, formula, $N-g_h$	Free energy		Enthalpy (heat contributions)				Entropy and heat capacity		
		$-\Delta_c G^0$ (Calc. ± 0.5) ^a	$-\Delta_f G^0$ (Calc. ± 0.5) ^b	$-\Delta_{\text{vap}} H^0$	$-\Delta_c H^0$	$-\Delta_f H^0$	$-\Delta_f H^0_{\text{gas}}$	S^0	$-\Delta_c S^0$ (Calc. ± 0.5) ^c	C_p
1	2	3	4	5	6	7	8	9	10	11
Nitrogen compounds										
I	Trimethylamine, C_3H_9N , 22	2410.6 ± 12.0	104.7 ± 0.5	22.0 ^[10] ± 0.1	2484.0 ^[11] ± 12.4	45.7 ^[10] ± 0.7	23.7 ^[10] ± 0.7	197.8 ^[12]	246.1 ± 1.2	132.5 ^[12]
II	Triethylamine, $C_6H_{15}N$, 40			34.9 ^[13] ± 0.1	4377.1 ^[14] ± 0.5	127.8 ^[14] ± 0.5	92.9 ^[14] ± 0.5			
III	Tri-n-ropylamine, $C_9H_{21}N$, 58			46.1 ^[13] ± 0.1	6335.7 ^[14] ± 0.8	206.9 ^[14] ± 0.8	160.8 ^[14] ± 0.8			
IV	Tri-n-butylamine, $C_{12}H_{27}N$, 76				8299.2 ^[14] ± 1.1	281.8 ^[14] ± 1.1				
V	Tri-n-hexylamine, $C_{18}H_{39}N$, 112				12223.8 ^[14] ± 1.5	433.0 ^[14] ± 1.8				
VI	Tri-n-octylamine, $C_{24}H_{51}N$, 148			110.0 ^[15] ± 15.0	16147.9 ^[14] ± 2.1	585.0 ^[14] ± 2.6	474.8 ^[14]			750.8 ^[15]
VII	Tri-n-nonylamine, $C_{27}H_{57}N$, 166				18109.3 ^[9] ± 1.7	661.6 ^[9] ± 2.3				
VIII	Tri-n-decylamine, $C_{30}H_{63}N$, 184				20070.9 ^[14] ± 3.1	738.0 ^[14] ± 3.6				
IX	Triphenylamine, $C_{18}H_{15}N$, 88			92.0 ^[16] ± 3.0	9462.0 ^[16] ± 3.0	235.0 ^[16] ± 3.0	-327.0 ^[16] ± 4.2			297.5 ^[17]
Phosphorus compounds										

No comp.	Title of Compound, formula, <i>N-gh</i>	Free energy		Enthalpy (heat contributions)			Entropy and heat capacity			
X	Trimethylphosphine, C ₃ H ₉ P, 22			28.5 ^[18] ±0.9	3194.9 ^[9] ±4.6	122.2 ^[9] ±4.6	94.1 ^[9] ±5.0			
XI	Triethylphosphine, C ₆ H ₁₅ P, 40			41.1 ^[18] ±2.0	5176.0 ^[9] ±12.5	89.1 ^[9] ±12.5	49.4 ^[9] ±13.0			
XII	Triphenylphosphine, C ₁₈ H ₁₅ P, 88			118.3 ^[18] ±0.6	10299.0 ^[9] ±12.5	-232.2 ^[9] ±19.2	-350.5 ^c ±19.8			
XIII	Pentaphenylphosphole, C ₃₄ H ₂₅ P, 162				18198.3 ^[9] ±28.4	-395.8 ^[9] ±28.4				
XIV	9-Phenyl-9-phosphafluorene, C ₁₈ H ₁₃ P, 86				9982.2 ^[9] ±16.7	-190.8 ^[9] ±16.7				
Arsenic compounds										
XV	Trimethylarsine, C ₃ H ₉ As, 22	2481.4 ±12.4	91.2 ±0.5	28.9 ^[9] ±1.2	2779.0 ^[9] ±10.0	16.3 ^[9] ±10.0	-11.7 ^[9] ±10.5	251.3 ^[19] ±5.0	998.1 ±5.0	154.0 ^[19]
XVI	Triethylarsine, C ₆ H ₁₅ As, 40			43.1 ^[9] ±4.2	4846.3 ^[9] ±16.7	-13.0 ^[9] ±16.7	-56.1 ^[9] ±17.6			234.3 ^[20]
XVII	Triphenylarsine, C ₁₈ H ₁₅ As, 88			123.6 ^[22] ±0.6	10082.6 ^[9] ±16.7	-393.3 ^[9] ±16.7	-516.9 ^c ±17.3			321.3 ^[21]
Stibium compounds										
XVIII	Trimethylstibine, C ₃ H ₉ Sb, 22			31.4 ^[9] ±1.3	2921.0 ^[9] ±25.1	-0.8 ^[9] ±25.1	-32.2 ^[9] ±25.1			
XIX	Triethylstibine, C ₆ H ₁₅ Sb, 40			43.5 ^[9] ±4.2	4864.3 ^[9] ±10.5	-5.0 ^[9] ±10.5	-48.5 ^[9] ±10.9			242.2 ^[23]
XX	Triphenylstibine, C ₁₈ H ₁₅ Sb, 88			106.3 ^[9] ±8.4	10009.8 ^[9] ±16.7	-329.3 ^[9] ±16.7	-435.5 ^[9] ±18.8			
Bismuth compounds										
XXI	Trimethylbismuthine, C ₃ H ₉ Bi, 22			36.0 ^[9] ±1.2	2912.1 ^[9] ±14.2	-158.2 ^[9] ±14.2	-192.9 ^[9] ±14.2			
XXII	Triethylbismuthine, C ₆ H ₁₅ Bi, 40	4687.9 ±23.4	-56.9 ±0.3	46.0 ^[9] ±4.2	4961.4 ^[9] ±16.7	-169.9 ^[9] ±16.7	-215.9 ^[9] ±17.6	379.0 ^[24] ±4.6	917.5 ±4.6	242.2 ^[24]
XXIII	Triphenylbismuthine, C ₁₈ H ₁₅ Bi, 88			110.9 ^[9] ±8.4	9983.0 ^[9] ±16.7	-469.0 ^[9] ±16.7	-579.9 ^[9] ±18.8			328.4 ^[21]
Oxygen compounds										
XXIV	Dimethyl ether, C ₂ H ₆ O, 12	1423.7 ±7.1	260.4 ±1.3	21.5 ^[25]	1460.4 ^[26] ±0.46		184.1 ^[26] ±0.50	146.6 ^[25]	124.0 ±0.6	102.3 ^[25]
XXV	Diethyl ether, C ₄ H ₁₀ O, 24	2670.6 ±13.3	346.8 ±1.7	27.4 ^[27]	2732.1 ^[28] ±1.9	271.2 ^[28] ±1.9	252.7 ^[29] ±2.0	253.5 ^[30]	206.4 ±1.0	172.5 ^[30]
XXVI	Di-n-propyl ether, n-C ₆ H ₁₄ O, 36	3915.0 ±19.6	367.8 ±1.8	35.7 ^[31]	4033.1 ^[32] ±0.79	328.8 ^[32] ±0.88	293.0 ^[32] ±2.0	323.9 ^[33]	396.3 ±2.0	221.6 ^[33]
XXVII	Di-iso-propyl ether, i-C ₆ H ₁₄ O, 36	3898.0 ±19.5	442.3 ±2.2	32.1 ^[31]	4010.4 ^[32] ±1.3	351.5 ^[32] ±1.4	318.0 ^[32] ±3.0	304.6 ^[33]	377.0 ±1.9	216.1 ^[33]
XXVIII	Di-n-Butyl ether, n-C ₈ H ₁₈ O, 48			45.0 ^[31]	5342.6 ^[32] ±0.92	378.0 ^[32] ±1.0	334.0 ^[32] ±2.0			278.2 ^[34]
XXIX	Di-sec-butyl ether, s-C ₈ H ₁₈ O, 48			40.6 ^[9] ±1.2	5319.0 ^[9] ±1.0	401.5 ^[9] ±1.2	360.9 ^[9] ±1.7			
XXX	Di-tert-Butyl ether, t-C ₈ H ₁₈ O, 48			37.6 ^[35] ±0.9	5322.1 ^[36] ±0.61	398.4 ^[36] ±0.72	361.1 ^[36] ±0.8			276.1 ^[35]
XXXI	Diphenyl ether, C ₁₂ H ₁₀ O, 56	6057.3 ±30.3	101.8 ±0.5	66.9 ^[37] ±0.3	6113.7 ^[38] ±3.8	32.1 ^[39] ±0.93		233.9 ^[39]	189.2 ±0.9	216.6 ^[39]
Sulfur compounds										
XXXII	Dimethyl sulfide, C ₂ H ₆ S, 12			27.9 ^[40] ±0.6	2181.5 ^[41] ±0.3	65.4 ^[40] ±1.5	37.5 ^[40] ±2.0			
XXXIII	Ethylmethyl sulfide, C ₂ H ₅ SCH ₃ , 18			32.0 ^[42] ±0.1	2833.6 ^[42] ±1.1	92.3 ^[42] ±1.1	60.3 ^[42] ±1.1			
XXXIV	Diethyl sulfide, C ₄ H ₁₀ S, 24	3380.6 ±16.9	199.6 ±1.0	35.8 ^[40] ±0.7	3486.1 ^[43] ±0.67	119.3 ^[40] ±0.72	83.5 ^[40] ±2.3	269.3 ^[44]	353.7 ±1.8	171.4 ^[44]

No comp.	Title of Compound, formula, <i>N-gh</i>	Free energy		Enthalpy (heat contributions)			Entropy and heat capacity			
XXXV	iso-Propylmethyl sulfide, $i\text{-C}_3\text{H}_7\text{SCH}_3$, 24	3377.2 ± 16.9	203.1 ± 1.0	35.0 ^[43]	3480.8 ^[43] ± 0.59	± 2.0 124.7 ^[43] ± 0.75	89.7 ^[43] ± 0.75	263.1 ^[45]	347.5 ± 1.7	172.4 ^[45]
XXXVI	n-Propylmethyl sulfide, $n\text{-C}_3\text{H}_7\text{SCH}_3$, 24			36.3 ^[46] ± 0.4				272.5 ^[46]		171.6 ^[46]
XXXVI I	n-Butylmethyl sulfide, $n\text{-C}_4\text{H}_9\text{SCH}_3$, 30	4017.4 ± 20.1	234.5 ± 1.2	40.8 ^d ± 0.3	4141.3 ^[47] ± 0.67	142.8 ^[47] ± 0.8	102.0 ^[47] ± 1.1	307.5 ^[47]	415.7 ± 2.1	200.9 ^[47]
XXXVI II	n-Propylethyl sulfide, $n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_5$, 30	4015.0 ± 20.1	236.9 ± 1.2	40.1 ^[47] ± 0.3	4139.5 ^[47] ± 0.59	144.6 ^[47] ± 0.75	104.5 ^[47] ± 0.8	309.5 ^[47]	417.7 ± 2.1	198.4 ^[47]
XXXIX	Di-n-propyl sulfide, $\text{C}_3\text{H}_7\text{SC}_3\text{H}_7$, 36	4654.1 ± 23.2	270.7 ± 1.3	44.6 ^[47]	4794.3 ^[47] ± 0.75	169.8 ^[47] ± 0.88	125.2 ^[47]	338.3 ^[47]	470.2 ± 2.3	225.5 ^[47]
XL	Di-iso-propyl sulfide, $i\text{-C}_3\text{H}_7\text{SC}_3\text{H}_7\text{-i}$, 36	4650.1 ± 23.2	274.4 ± 1.4	39.6 ^[48] ± 0.2	4782.8 ^[48] ± 0.84	181.1 ^[48] ± 0.96	142.0 ± 1.3	313.0 ^[49]	444.9 ± 2.2	232.0 ^[49]
XLI	Diphenyl sulfide, $\text{C}_6\text{H}_5\text{SC}_6\text{H}_5$, 56			68.0 ^[50] ± 2.0	6916.9 ^[50] ± 2.0	-163.8 ^[50] ± 2.0	-232.0 ^[50] ± 3.0			271.1 ^[17]
Fluor compounds										
XLII	Fluorobenzene, $\text{C}_6\text{H}_5\text{F}$, 24			34.6 ^[51]	3103.9 ^[52] ± 1.2	150.8 ^[52] ± 1.4		205.9 ^[51]		146.4 ^[51]
XLIII	1-Fluoro-4-methylbenzene, $\text{C}_7\text{H}_7\text{F}$, 30			39.4 ^[53] ± 0.08	3747.2 ^[53] ± 0.71	186.9 ^[53] ± 0.08	147.5 ^[53] ± 0.08	237.1 ^[54]		171.2 ^[54]
XLIV	1,4-Difluorobenzene, $\text{C}_6\text{H}_4\text{F}_2$, 26			35.6 ^[53] ± 0.2	2948.4 ^[53] ± 0.54	342.3 ^[53] ± 1.0	306.7 ^[53] ± 1.0			157.5 ^[53]
XLV	1,3-Difluorobenzene, $\text{C}_6\text{H}_4\text{F}_2$, 26			34.7 ^[53] ± 0.2	2946.7 ^[53] ± 0.71	343.9 ^[53] ± 1.0	309.2 ± 1.0	223.8 ^[55]		159.1 ^[55]
XLVI	1,2-Difluorobenzene, $\text{C}_6\text{H}_4\text{F}_2$, 26			36.2 ^[53] ± 0.08	2960.7 ^[53] ± 0.54		283.0 ^[53] ± 0.92	222.6 ^[56]		159.4 ^[53]
XLVII	1-Fluoroheptane, $\text{C}_7\text{H}_{15}\text{F}$, 38				4692.4 ^[57]					
XLVIII	1-Fluorooctane, $\text{C}_8\text{H}_{17}\text{F}$, 44			49.7 ^[27]	5318.0 ^[57]					
XLIX	1,1-Difluoroethane, $\text{C}_2\text{H}_4\text{F}_2$, 8				1220.0 ^[58] ± 8.4		497.0 ^[58] ± 4.0			
Chlor compounds										
L	Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, 24			41.0 ^[59] ± 0.06	3112.7 ^[60] ± 0.9	-11.5 ^[61] ± 1.0	-54.4 ^[60]	197.5 ^[62]		152.1 ^[63]
LI	n-Propylchloride, $\text{C}_3\text{H}_7\text{Cl}$, 14			28.6 ^[27]	2025.0 ^[64] ± 8.0		132.5 ^[65] ± 0.92			132.2 ^[66]
LII	2-Chloropropane, $\text{C}_3\text{H}_7\text{Cl}$, 14			27.2 ^[67] ± 0.84	2028.4 ^[64] ± 8.4		144.0 ^d ± 5.0			
LIII	1-Chlorobutane, $\text{C}_4\text{H}_9\text{Cl}$, 20			33.5 ^[59] ± 0.06	2695.8 ^[68] ± 1.1	188.2 ^[68] ± 1.2	154.6 ^[68] ± 1.2			158.9 ^[70]
LIV	2-Chlorobutane, $\text{C}_4\text{H}_9\text{Cl}$, 20			31.6 ^[59] ± 0.06	2685.5 ^[69] ± 0.95	198.4 ^[69] ± 0.99	166.7 ^[69] ± 0.99			160.9 ^[70]
LV	2-Chloro-2-methylpropane, $\text{C}_4\text{H}_9\text{Cl}$, 20			29.2 ^[27]	2675.2 ^[64] ± 8.4	211.2 ^[71] ± 2.3	179.9 ^[72]			162.0 ^[70]
LVI	1-Chlorooctane, $\text{C}_8\text{H}_{17}\text{Cl}$, 44			52.4 ^[59] ± 0.12	5310.0 ^[68] ± 1.8	291.3 ^[68] ± 1.9	238.9 ^[68] ± 1.9			274.7 ^[70]
LVII	1-Chlorohexane, $\text{C}_6\text{H}_{13}\text{Cl}$, 32			42.8 ^[59] ± 0.06						216.2 ^[70]
LVIII	Chlorocyclohexane, $\text{C}_6\text{H}_{11}\text{Cl}$, 30			42.7 ^[73] ± 0.03	3747.6 ^[73] ± 1.9	209.1 ^[73] ± 1.9	166.5 ^[73] ± 1.9			

No comp.	Title of Compound, formula, <i>N-gh</i>	Free energy	Enthalpy (heat contributions)			Entropy and heat capacity	
Brom compounds							
LIX	Bromobenzene, C ₆ H ₅ Br, 24		44.5 ^[59] ±0.04	3111.9 ^[74] ±0.67	60.9 ^[75] ±4.1	219.2 ^[76]	154.3 ^[76]
LX	Ethylbromide, C ₂ H ₅ Br, 8		28.3 ^[27]		105.8 ^[70]	63.6 ^[77]	
LXI	n-Propylbromide, C ₃ H ₇ Br, 14		31.9 ^[27] ±0.08	2056.6 ^[78] ±1.4	124.4 ^[78] ±1.4	82.9 ^[79]	134.6 ^[70]
LXII	2-Bromopropane, C ₃ H ₇ Br, 14		30.3 ^[27]	2051.9 ^[78] ±1.8	129.1 ^[78] ±1.8	95.6 ^[79] ±1.0	135.6 ^[70]
LXIII	1-Bromobutane, C ₄ H ₉ Br, 20		36.6 ^[59] ±0.10	2716.5 ^[78] ±1.3	143.8 ^[78] ±1.3	107.0 ^[78] ±2.0	162.2 ^[70]
LXIV	1-Bromo-2-methylpropane, C ₄ H ₉ Br, 20		34.9 ^[59] ±0.02		160.0 ^[82] ±0.8		163.7 ^[70]
LXV	2-Bromobutane, C ₄ H ₉ Br, 20		34.5 ^[59] ±0.06	2705.0 ^[78] ±1.0	155.3 ^[78] ±1.3	120.0 ^[78] ±2.0	
LXVI	1-Bromooctane, C ₈ H ₁₇ Br, 44		55.8 ^[80] ±0.25	5332.6 ^[78] ±2.3	245.2 ^[78] ±2.3	190.1 ^[78] ±2.3	
Iod compounds							
LXVII	Iodobenzene, C ₆ H ₅ I, 24		47.7 ^[81] ±4.2	3192.8 ^[81] ±4.2	-117.0 ^[81] ±4.2	-165.0 ^[81] ±5.9	205.4
LXVIII	1-Iodo-4-methylbenzene, C ₇ H ₇ I, 30		54.4 ^[81] ±4.2	3822.5 ^[81] ±4.2	-67.4 ^[81] ±4.2	-122.0 ^[81] ±5.9	
LXXIX	1-Iodo-3-methylbenzene, C ₇ H ₇ I, 30		54.4 ^[81] ±4.2	3834.2 ^[81] ±4.2	-79.1 ^[81] ±4.2	-133.0 ^[81] ±5.9	
LXX	Iodoethane, C ₂ H ₅ I, 8		31.9 ^[59] ±0.02	1462.5 ^[84] ±0.4	39.1 ^[84] ±0.8	7.2 ^[84] ±0.8	109.7 ^[70]
LXXI	1-Iodobutane, C ₄ H ₉ I, 20		40.6 ^[59] ±0.04				164.5 ^[70]
LXXII	Iodocyclohexane, C ₆ H ₁₁ I, 30		43.1 ^[85] ±0.8	3835.9 ^[81] ±4.2			

^a Calc. through Eq. (13); ^b Calc. through Eq. (14); ^c Calc. as difference: $\Delta_r H^{\circ}_{\text{cond}} - \Delta_{\text{vap}} H^{\circ}$; ^d Average of 6 values; ^e Calc. through Eq. (12).

2.2. Organic Compounds of VIth Group (Ethers and Sulfides)

The thermodynamic data of ethers and sulfides are presented most full among heteroatomic compounds of VIth group. There is an opportunity to analyze all thermodynamic functions and heat capacity of compounds

(XXIV-XLI, Table 1). First of all we shall carry out the research of the heats of vaporization of ethers (XXIV-XXXI). The received equation (31) shows a good dependence of $\Delta_{\text{vap}} H^{\circ}$ of ethers on the number of valence electrons (*N-g*). The similar dependence (32) is received for the heats of vaporization of sulfides (XXXII-XLI, Table 2)

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

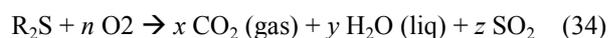
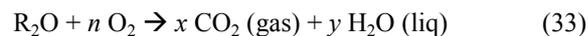
The functions of processes	No Eq. in text	<i>i</i>	<i>f</i>	<i>r</i>	<i>S_o</i>	Nos. of compounds in Table 1
1	2	3	4	5	6	7
Nitrogen compounds						
$\Delta_{\text{vap}} H^{\circ}$	2	8.3 ± 10.4	0.7 ± 0.1	0.960	11.2	I-III, VI, IX
$\Delta_c H^{\circ}$	6	-21.8 ± 41.6	-108.8 ± 0.4	0.999	59.5	I-IX
$\Delta_f H^{\circ}_{\text{cond}}$	8	57.8 ± 23.9	-4.3 ± 0.2	0.991	34.1	I-IX
$\Delta_f H^{\circ}_{\text{gas}}$	9	50.4 ± 4.0	-3.5 ± 0.04	0.999	4.7	I-III, VI
Phosphorus compounds						
$\Delta_{\text{vap}} H^{\circ}$	3	-8.4 ± 10.8	1.4 ± 0.2	0.991	9.1	X-XII
$\Delta_c H^{\circ}$	7	-854.8 ± 45.4	-107.0 ± 0.5	0.999	52.8	X-XIV
$\Delta_f H^{\circ}_{\text{cond}}$	10	-191.5 ± 58.2	3.9 ± 0.6	0.964	67.7	X-XIV
$\Delta_f H^{\circ}_{\text{gas}}$	11	-284.3 ± 71.7	7.1 ± 1.2	0.985	60.4	X-XII
Arsenic compounds						
$\Delta_{\text{vap}} H^{\circ}$	15	-9.0 ± 10.8	1.5 ± 0.2	0.992	9.2	XV-XVII
$\Delta_c H^{\circ}$	21	-385.8 ± 70.7	-110.3 ± 1.2	0.999	59.6	XV-XVII
$\Delta_f H^{\circ}_{\text{cond}}$	22	-198.0 ± 77.2	6.6 ± 1.3	0.979	65.1	XV-XVII
$\Delta_f H^{\circ}_{\text{gas}}$	23	-207.9 ± 87.5	8.0 ± 1.5	0.982	73.7	XV-XVII

The functions of processes	No Eq. in text	<i>i</i>	<i>f</i>	<i>r</i>	<i>S₀</i>	Nos. of compounds in Table 1
<i>C_p</i>	30	117.2 ± 32.5	2.3 ± 0.6	0.973	27.4	XV-XVII
Stibium compounds						
$\Delta_{\text{vap}}H^{\circ}$	16	1.9 ± 7.8	1.2 ± 0.1	0.993	6.6	XVIII-XX
$\Delta_{\text{c}}H^{\circ}$	24	-528.6 ± 34.6	-107.8 ± 0.6	0.999	29.2	XVIII-XX
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	25	-155.5 ± 80.0	5.3 ± 1.4	0.967	67.4	XVIII-XX
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	26	-152.6 ± 88.4	6.5 ± 1.5	0.973	74.6	XVIII-XX
Bismuth compounds						
$\Delta_{\text{vap}}H^{\circ}$	17	5.3 ± 9.8	1.2 ± 0.2	0.990	8.2	XXI-XXIII
$\Delta_{\text{c}}H^{\circ}$	27	-621.4 ± 113.2	-106.6 ± 2.0	0.999	95.4	XXI-XXIII
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	28	14.5 ± 68.4	5.0 ± 1.2	0.973	57.7	XXI-XXIII
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	29	18.6 ± 77.3	6.2 ± 1.3	0.977	65.2	XXI-XXIII
Oxygen compounds						
$\Delta_{\text{c}}G^{\circ}$	46	-143.0 ± 29.3	-105.2 ± 0.8	0.999	26.7	XXIV-XXXVII, XXXI
$\Delta_{\text{f}}G^{\circ}_{\text{cond}}$	47	-194.5 ± 55.2	-5.9 ± 1.9	0.909	38.2	XXIV-XXXVII
$\Delta_{\text{vap}}H^{\circ}$	31	14.5 ± 3.0	0.5 ± 0.1	0.953	2.6	XXIV-XXXI
$\Delta_{\text{c}}H^{\circ}$	35	-180.0 ± 28.4	-106.8 ± 0.7	0.999	26.9	XXIV-XXXI
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	37	-157.9 ± 24.1	-4.9 ± 0.6	0.973	12.9	XXV-XXX
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	38	-137.4 ± 15.7	-4.5 ± 0.4	0.980	14.0	XXIV-XXX
<i>S_{cond}</i>	41	73.3 ± 24.5	6.8 ± 0.8	0.985	16.9	XXIV-XXX
$\Delta_{\text{c}}S^{\circ}_{\text{cond}}$	45	29.6 ± 44.9	-11.3 ± 1.5	0.981	31.0	XXIV-XXXVII
<i>C_p</i>	42	59.1 ± 6.4	4.7 ± 0.2	0.997	5.5	XXIV-XXXVIII, XXX
Sufur compounds						
$\Delta_{\text{c}}G^{\circ}$	49	-832.7 ± 3.3	-106.1 ± 0.1	0.999	1.3	XXXIV, XXXV, XXXVII-XL
$\Delta_{\text{f}}G^{\circ}_{\text{cond}}$	50	-58.5 ± 5.4	-5.9 ± 0.2	0.998	2.1	XXXIV, XXXV, XXXVII-XL
$\Delta_{\text{vap}}H^{\circ}$	32	14.7 ± 2.6	0.9 ± 0.1	0.964	3.1	XXXII-XLI
$\Delta_{\text{c}}H^{\circ}$	36	-876.9 ± 5.1	-108.7 ± 0.2	0.999	4.1	XXXII-XXXV, XXXVII-XL
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	39	-11.4 ± 5.4	-4.5 ± 0.2	0.994	4.4	XXXII-XXXV, XXXVII-XL
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	40	9.8 ± 7.5	-3.9 ± 0.3	0.985	6.1	XXX-XXXV, XXVII-XL
<i>S_{cond}</i>	43	153.6 ± 23.6	4.9 ± 0.8	0.940	10.5	XXXIV, XXXV-XL
$\Delta_{\text{c}}S^{\circ}_{\text{cond}}$	48	-140.9 ± 29.8	-8.9 ± 1.0	0.977	11.8	XXXIV, XXXV, XXXVI, XXXVII-XL
<i>C_p</i>	44	100.8 ± 11.4	3.2 ± 0.3	0.969	9.5	XXXIV-XLI
Fluor compounds						
$\Delta_{\text{vap}}H^{\circ}$	57	15.5 ± 1.2	0.8 ± 0.04	0.995	0.7	XLII-XLIX
$\Delta_{\text{c}}H^{\circ}$	58	-135.3 ± 202.1	-116.5 ± 6.8	0.990	192.5	XLII-XLIX
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	59	-619.8 ± 72.8	13.4 ± 3.0	0.933	51.6	XLIII- XLVI, XLIX
<i>S_{cond}</i>	60	94.2 ± 29.2	4.8 ± 1.1	0.952	4.8	XLII, XLIII, XLV, XLVI
<i>C_p</i>	61	56.2 ± 15.6	3.9 ± 0.6	0.967	2.6	XLII-XLVI
Chlor compounds						
$\Delta_{\text{vap}}H^{\circ}$	62	15.9 ± 2.3	0.8 ± 0.1	0.964	2.4	L-LVIII
$\Delta_{\text{c}}H^{\circ}$	63	-498.4 ± 12.4	-109.1 ± 0.5	0.999	13.0	L-LVI, LXVIII
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	64	-122.4 ± 23.3	-3.6 ± 0.8	0.931	17.3	LIII-LVI, LVIII
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	65	-100.1 ± 14.7	-3.0 ± 0.6	0.915	15.2	LI-LVI, LVIII
<i>C_p</i>	66	60.9 ± 12.2	4.8 ± 0.5	0.977	11.3	L, LI, LIII-LVII
Brom compounds						
$\Delta_{\text{vap}}H^{\circ}$	67	20.4 ± 1.9	0.8 ± 0.1	0.970	2.3	LIX-LXVI
$\Delta_{\text{c}}H^{\circ}$	68	-520.6 ± 16.7	-109.2 ± 0.7	0.999	16.7	LIX, LXI-LXIII, LXV, LXVI
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	69	-73.8 ± 4.5	-3.9 ± 0.2	0.993	5.6	LX-LXVI
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	70	-41.0 ± 6.1	-3.4 ± 0.3	0.988	7.4	LX-LXIII, LXV, LXIV
<i>C_p</i>	71	70.1 ± 2.6	4.6 ± 0.1	0.999	0.9	LXI-LXIV
Iod compounds						
$\Delta_{\text{vap}}H^{\circ}$	72	22.4 ± 2.3	1.0 ± 0.1	0.987	1.8	LXVII-LXXII
$\Delta_{\text{c}}H^{\circ}$	73	-603.0 ± 9.8	107.6 ± 0.4	0.999	7.3	LXVII-LXX, LXXII
$\Delta_{\text{f}}H^{\circ}_{\text{cond}}$	74	-79.9 ± 11.5	5.1 ± 0.5	0.996	8.3	LXVIII-LXX
$\Delta_{\text{f}}H^{\circ}_{\text{gas}}$	75	-56.2 ± 10.8	6.1 ± 0.4	0.997	7.8	LXVIII-LXX
<i>C_p</i>	76	85.2 ± 22.4	3.5 ± 1.2	0.943	14.1	LXVII, LXX, LXXI

$$\Delta_{\text{vap}}H^{\circ} = (14.5 \pm 3.0) + (0.5 \pm 0.1) (N - hg) \quad r 0.953, S_0 2.6, n 8 \text{ (compounds XXIV-XXXI)} \quad (31)$$

$$\Delta_{\text{vap}}H^{\circ} = (14.7 \pm 2.6) + (0.9 \pm 0.1) (N - hg) \quad r 0.964, S_0 3.1, n 10 \text{ (compounds XXXII-XLI)} \quad (32)$$

The processes of combustion of both types the given above compounds are characterized by schemes (33 и 34)



On the basis of known data on the heats of combustion of ethers and sulfides (Table 1) the equations (35 and 36) have been received (Table 2)

$$\Delta_c H^\circ = (-180.0 \pm 28.4) - (106.8 \pm 0.7) (N - hg) \quad r \ 0.999, S_o \ 26.9, n \ 8 \text{ (compounds XXIV-XXXI)} \quad (35)$$

$$\Delta_c H^\circ = (-876.9 \pm 5.1) - (108.7 \pm 0.2) (N - hg) \quad r \ 0.999, S_o \ 4.1, n \ 9 \text{ (compounds XXXII-XXXV, XXXVII-XL)} \quad (36)$$

The same conclusion can be made concerning the heats of formation of ethers (Eqs. 37 and 38) and sulfides (Eqs. 39 and 40) in the condensed and gas phases also

$$\Delta_f H^\circ_{\text{cond}} = (-157.9 \pm 24.1) - (4.9 \pm 0.6) (N - hg) \quad r \ 0.973, S_o \ 12.9, n \ 6 \text{ (compounds XXV-XXX)} \quad (37)$$

$$\Delta_f H^\circ_{\text{gas}} = (-137.4 \pm 15.7) - (4.5 \pm 0.4) (N - hg) \quad r \ 0.980, S_o \ 14.0, n \ 7 \text{ (compounds XXIV-XXX)} \quad (38)$$

$$\Delta_f H^\circ_{\text{cond}} = (-11.4 \pm 5.4) - (4.5 \pm 0.2) (N - hg) \quad r \ 0.994, S_o \ 4.4, n \ 8 \text{ (compounds XXXII-XXXV, XXXVII-XL)} \quad (39)$$

$$\Delta_f H^\circ_{\text{gas}} = (9.8 \pm 7.5) - (3.9 \pm 0.3) (N - hg) \quad r \ 0.985, S_o \ 6.1, n \ 8 \text{ (compounds XXXII-XXXV, XXXVII-XL)} \quad (40)$$

The experimental values of entropy of formation and heat capacity in condensed phase for ethers (XXIV-XXVIII, XXX, XXXI) and sulfides (XXXIV-XLI) are known in the literature (Table 1), that has enabled to calculate the equations (41 and 42) for ethers and the equations (43 and 44) for sulfides.

$$S^\circ_{\text{cond}} = (73.3 \pm 24.5) + (6.8 \pm 0.8) (N - hg) \quad r \ 0.985, S_o \ 16.9, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (41)$$

$$C_p = (59.1 \pm 6.4) + (4.7 \pm 0.2) (N - hg) \quad r \ 0.997, S_o \ 5.5, n \ 6 \text{ (compounds XXIV-XXVIII, XXX)} \quad (42)$$

$$S^\circ_{\text{cond}} = (153.6 \pm 23.5) + (4.9 \pm 0.8) (N - hg) \quad r \ 0.940, S_o \ 10.5, n \ 7 \text{ (compounds XXXIV-XL)} \quad (43)$$

$$C_p = (100.8 \pm 11.4) + (3.2 \pm 0.3) (N - hg) \quad r \ 0.969, S_o \ 9.5, n \ 8 \text{ (compounds XXXIV-XLI)} \quad (44)$$

With the use of Eqs. (12-14) the entropies of combustion, free energies of combustion and formation in condensed state of ethers and sulfides have been calculated (Table 1) and have allowed to produce the Eqs. (45-50, Table 2) correspondingly.

$$\Delta_c S^\circ_{\text{cond}} = (29.6 \pm 44.9) - (11.3 \pm 1.5) (N - hg) \quad r \ 0.981, S_o \ 31.0, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (45)$$

$$\Delta_c G^\circ = (-143.0 \pm 29.3) - (105.2 \pm 0.8) (N - hg) \quad r \ 0.999, S_o \ 26.7, n \ 5 \text{ (compounds XXIV-XXVII, XXXI)} \quad (46)$$

$$\Delta_f G^\circ_{\text{cond}} = (-194.5 \pm 55.2) - (5.9 \pm 1.9) (N - hg) \quad r \ 0.909, S_o \ 38.2, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (47)$$

$$\Delta_c S^\circ_{\text{cond}} = (-140.9 \pm 29.8) - (8.9 \pm 1.0) (N - hg) \quad r \ 0.977, S_o \ 11.8, n \ 4 \text{ (compounds XXIV, XXXV, XXXVI, XXXVII-XL)} \quad (48)$$

$$\Delta_c G^\circ = (-832.7 \pm 3.3) - (106.1 \pm 0.1) (N - hg) \quad r \ 0.999, S_o \ 1.3, n \ 6 \text{ (compounds XXXIV, XXXV, XXXVII-XL)} \quad (49)$$

$$\Delta_f G^\circ_{\text{cond}} = (-58.5 \pm 5.4) - (5.9 \pm 0.2) (N - hg) \quad r \ 0.998, S_o \ 2.1, n \ 6 \text{ (compounds XXXIV, XXXV, XXXVII-XL)} \quad (50)$$

Necessary to add, that the calculated thermodynamic functions are in a good dependencies among themselves: for ethers it Eqs. (51-53), and for sulfides it (54-56).

$$\Delta_f H^\circ_{\text{cond}} = (-11.4 \pm 5.4) - (4.5 \pm 0.2) S^\circ_{\text{cond}} \quad r \ 0.949, S_o \ 23.6, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (51)$$

$$S^\circ_{\text{cond}} = (100.5 \pm 40.9) - (0.6 \pm 0.1) C_p \quad r \ 0.946, S_o \ 31.4, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (52)$$

$$\Delta_c H^\circ = (-547.2 \pm 362.7) + (9.1 \pm 1.2) \Delta_c S^\circ_{\text{cond}} \quad r \ 0.982, S_o \ 279.2, n \ 4 \text{ (compounds XXIV-XXVII)} \quad (53)$$

$$\Delta_f H^\circ_{\text{cond}} = (44.1 \pm 25.7) - (0.6 \pm 0.1) S^\circ_{\text{cond}} \quad r \ 0.972, S_o \ 5.4, n \ 6 \text{ (compounds XXXIV, XXXV, XXXVII-XL)} \quad (54)$$

$$\Delta_c H^\circ = (615.7 \pm 506.7) + (11.6 \pm 1.2) \Delta_c S^\circ_{\text{cond}} \quad r \ 0.978, S_o \ 135.3, n \ 6 \text{ (compounds XXXIV, XXXV, XXXVII-XL)} \quad (55)$$

$$S^\circ_{\text{cond}} = (100.0 \pm 39.3) + (1.0 \pm 0.2) C_p \quad r \ 0.914, S_o \ 12.5, n \ 7 \text{ (compounds XXXIV-XL)} \quad (56)$$

2.3. Organic Compounds of VIIth Group (Fluorides, Bromides and Iodides)

The thermodynamic parameters (the heats of vaporization, combustion, formation, entropy of formation and heat capacities) of halogen-containing organic compounds can be used in the calculations relatively to the number of their valence electrons only. Such situation has turned out, as processes of combustion of fluorides,

bromines and iodides the various authors characterize differently: with formation water-containing HF, HCl and HBr of a various structure or gaseous HI and crystalline I₂ [9]. It does not give an opportunity to make calculations of entropy of combustion and free energies, as in the literature there are no data on entropy of formation the corresponding combustion products, which are necessary for the equation (12).

For this reason the calculations of the heats of vaporization, combustion, formation, entropy of formation and heat capacity (Table 1) have been made for compounds (XLII-LXXII) only (Eqs. 57-76, Table 2):

For fluorides:

$$\Delta_{\text{vap}}H^{\circ} = (15.5 \pm 1.2) + (0.8 \pm 0.04) (N - hg) \quad r 0.995, S_0 0.7, n 6 \text{ (compounds XLII-XLIX)} \quad (57)$$

$$\Delta_{\text{c}}H^{\circ} = (-135.3 \pm 202.1) - (116.5 \pm 6.8) (N - hg) \quad r 0.990, S_0 192.5, n 8 \text{ (compounds XLII-XLIX)} \quad (58)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{gas}} = (-619.8 \pm 72.8) + (13.4 \pm 3.0) (N - hg) \quad r 0.933, S_0 51.6, n 5 \text{ (compounds XLIII-XLVI, XLXIX)} \quad (59)$$

$$S^{\circ}_{\text{cond}} = (94.2 \pm 29.2) + (4.8 \pm 1.1) (N - hg) \quad r 0.952, S_0 4.8, n 4 \text{ (compounds XLII, XLIII, XLV, XLVI)} \quad (60)$$

$$C_p = (56.2 \pm 15.6) + (3.9 \pm 0.6) (N - hg) \quad r 0.967, S_0 2.6, n 5 \text{ (compounds XLII-XLVI)} \quad (61)$$

For chlorides:

$$\Delta_{\text{vap}}H^{\circ} = (15.9 \pm 2.3) + (0.8 \pm 0.1) (N - hg) \quad r 0.964, S_0 2.4, n 9 \text{ (compounds L-LVIII)} \quad (62)$$

$$\Delta_{\text{c}}H^{\circ} = (-498.4 \pm 12.4) - (109.1 \pm 0.5) (N - hg) \quad r 0.999, S_0 13.0, n 8 \text{ (compounds L-LVI, LXVIII)} \quad (63)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{cond}} = (-122.4 \pm 23.3) - (3.6 \pm 0.8) (N - hg) \quad r 0.931, S_0 17.3, n 5 \text{ (compounds LIII-LVI, LVIII)} \quad (64)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{gas}} = (-100.1 \pm 14.7) - (3.0 \pm 0.6) (N - hg) \quad r 0.915, S_0 15.2, n 7 \text{ (compounds LI-LVI, LVIII)} \quad (65)$$

$$C_p = (60.9 \pm 12.2) + (4.8 \pm 0.5) (N - hg) \quad r 0.977, S_0 11.3, n 7 \text{ (compounds L, LI, LIII-LVII)} \quad (66)$$

For bromines:

$$\Delta_{\text{vap}}H^{\circ} = (20.4 \pm 1.9) + (0.8 \pm 0.1) (N - hg) \quad r 0.970, S_0 2.3, n 8 \text{ (compounds LIX-LXVI)} \quad (67)$$

$$\Delta_{\text{c}}H^{\circ} = (-520.6 \pm 1.6) - (109.2 \pm 0.7) (N - hg) \quad r 0.999, S_0 16.7, n 6 \text{ (compounds LIX, LXI-LXIII, LXV, LXVI)} \quad (68)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{cond}} = (-73.8 \pm 4.5) - (3.9 \pm 0.2) (N - hg) \quad r 0.993, S_0 5.6, n 7 \text{ (compounds LX-LXVI)} \quad (69)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{gas}} = (-41.0 \pm 6.1) - (3.4 \pm 0.3) (N - hg) \quad r 0.988, S_0 7.4, n 6 \text{ (compounds LX-LXIII, LXV, LXVI)} \quad (70)$$

$$C_p = (70.1 \pm 2.6) + (4.6 \pm 0.1) (N - hg) \quad r 0.999, S_0 0.9, n 4 \text{ (compounds LXI-LXIV)} \quad (71)$$

For iodines:

$$\Delta_{\text{vap}}H^{\circ} = (22.4 \pm 2.3) + (1.0 \pm 0.1) (N - hg) \quad r 0.987, S_0 1.8, n 6 \text{ (compounds LXVII-LXXII)} \quad (72)$$

$$\Delta_{\text{c}}H^{\circ} = (-603.0 \pm 9.8) - (107.6 \pm 0.4) (N - hg) \quad r 0.999, S_0 7.3, n 5 \text{ (compounds LXVII-LXX, LXXII)} \quad (73)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{cond}} = (-79.9 \pm 11.5) + (5.1 \pm 0.5) (N - hg) \quad r 0.996, S_0 7.8, n 3 \text{ (compounds LXVIII-LXX)} \quad (74)$$

$$\Delta_{\text{f}}H^{\circ}_{\text{gas}} = (-56.2 \pm 10.8) + (6.1 \pm 0.4) (N - hg) \quad r 0.997, S_0 7.8, n 3 \text{ (compounds LXVIII-LXX)} \quad (75)$$

$$C_p = (85.2 \pm 22.4) + (3.4 \pm 1.2) (N - hg) \quad r 0.943, S_0 14.1, n 3 \text{ (compounds LXVII, LXX, LXXI)} \quad (76)$$

The available thermodynamic data have allowed to receiving one dependence (77) for fluorine

$$S^{\circ}_{\text{cond}} = (22.1 \pm 10.2) + (1.2 \pm 0.1) C_p \quad r 0.997, S_0 1.1, n 4 \text{ (compounds XLII, XLIII, XLV, XLVI)} \quad (77)$$

3. Conclusion

The analysis of thermodynamic functions and heat capacities of organic compounds of V-VII groups of Mendeleev's Periodic system allows making a some essential conclusions.

- The most significant conclusion is the successful application of the equation (1) for an estimation of the interrelation of all functions with a number of valence electrons without taking into account of lone electrons pairs.

- The stoichiometric coefficients, which have been deduced for the vaporization processes and heat capacities,

to characterize difficultly enough. It is necessary to note only, that in all cases they reflect partially a various spatial structure of the investigated compounds.

- The contributions from free energy and entropy of combustion and formation are calculated only for oxygen, sulfur and partly fluorine compounds. For this reason their analysis causes the certain difficulties. Analyzing the data of Table 2 it is possible to add only, that f coefficients in equation (1) for free energies of combustion are very close to such coefficients for the heat of combustion processes.

- It has been found, that calculated thermodynamic functions of ethers and sulfides are in good

interdependence from each other: $\Delta_c H^\circ - \Delta_c S^\circ_{\text{cond}}, \Delta H_f^\circ - S^\circ_{\text{cond}}, S^\circ_{\text{cond}} - C_p$.

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