ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2009, Vol. 54, No. 2, pp. 252–259. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © P.G. Sennikov, S.K. Ignatov, A.E. Sadov, A.G. Razuvaev, O. Schrems, 2009, published in Zhurnal Neorganicheskoi Khimii, 2009, Vol. 54, No. 2, pp. 287–294.

ELECTRONIC STRUCTURE

Quantum-Chemical Calculation of the Thermodynamics of Multistep Hydrolysis of MX_4 Molecules (M = C, Si, Ge; X = H, F, Cl) in the Gas Phase

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Received December 4, 2007

Abstract—The standard enthalpies, entropies, and Gibbs free energies of separate stages of the multistep hydrolysis of MX_4 molecules (M = C, Si, Ge; X = H, F, Cl) in the gas phase at 298 K were calculated by the G3 high-precision quantum-chemical method of calculation of thermodynamic parameters. The trends in these parameters were analyzed for each group of molecules. The calculated thermodynamic parameters make it possible to estimate the theoretical limits for the contents of water and hydrolysis products in the above high-purity carbon, silicon, and germanium derivatives.

DOI: 10.1134/S0036023609020144

The family of MX_4 molecules (M = C, Si, Ge; X = H, F, Cl) includes methane and carbon tetrachloride, very important in chemistry, and compounds structurally related to them (CF_4, SiH_4, $SiCl_4$, SiF_4, GeH_4, $GeCl_4$, GeF_4), which have attracted much attention in the past decades due to their use for preparing new inorganic materials.

Interaction with water is among the fundamental reactions in the chemistry of these compounds. The scheme of methane steam reforming, in which methane reacts with steam in the presence of a catalyst to yield CO and hydrogen, is universally known [1]. Tetrafluoromethane does not react with water in the absence of a catalyst even on heating to 500°C and a pressure of 4000 atm [2]; but it is hydrolyzed to CO_2 and hydrogen fluoride at atmospheric pressure and 900°C over metal oxides supported on alumina [3]. Carbon tetrachloride reacts with water to form CO_2 and hydrogen chloride at 300°C and 10 atm [4]. According to high-resolution IR spectroscopy evidence, no changes are observed for a rather long time in a 1 : 1 mixture of silane and water at a pressure of 20 mmHg in a cell [5]. No information on the specific features of the reaction of germane with water is available. The reaction with water of volatile silicon and germanium chlorides and fluorides in the gas phase at elevated temperature (sometimes in a burner flame or plasma discharge) is of practical significance for the synthesis of high-purity oxides of these elements and semiconducting silicon and germanium per se and for the disposal of waste of hazardous industries using fluoride technologies [6–10]. At the same time, it is well known that, as distinct from halomethanes and silane, silicon and germanium halides readily react with atmospheric moisture even at room temperature: the reaction yields gaseous HCl or HF and fine SiO_2.

The complete hydrolysis of MX_4 proceeds by the schemes

$$MX_4 + 2H_2O \rightleftharpoons MO_2 + 4H_2, \quad (1)$$

$$MX_4 + 2H_2O \rightleftharpoons MO_2 + 4HX. \quad (2)$$

For CH_4, SiH_4, and GeH_4 molecules, scheme (1) is valid; and scheme (2) is valid for CCl_4, CF_4, $SiCl_4$, SiF_4, $GeCl_4$, and GeF_4. In the second case, for M = Si and Ge, heterogeneous processes resulting in formation of a solid oxides are, as a rule, considered. The mechanisms of reactions (1) and (2), i.e., the composition of intermediate compounds and their stability and rate of further transformation, have been studied only in some cases and even then inadequately. Generally, for overall reactions (1) or (2), the following sequence of transformations can be suggested [6]: If the H_2O/MX_4 ratio is small,

$$MX_4 + H_2O \rightleftharpoons MX_3OH + HX \quad \text{(primary hydrolysis)}, \quad (3)$$

$$MX_3OH + MX_4 \rightleftharpoons MX_3{-}O{-}MX_3 + HX \quad \text{(condensation)}, \quad (4)$$

$$2MX_3OH \rightleftharpoons MX_3\text{–}O\text{–}MX_3 + H_2O \text{ (condensation)}, \quad (5)$$

$$MX_3\text{–}O\text{–}MX_3 + H_2O \rightleftharpoons MX_3\text{–}O\text{–}MX_2(OH) \text{ (chain growth and cyclization)}. \quad (6)$$

The reactions can yield linear $X(\text{–}MX_2\text{–}O\text{–})_nH$ and cyclic $(\text{–}MX_2\text{–}O\text{–})_n$ polymers.

If the H_2O/MX_4 ratio is rather high, primary hydrolysis (3) is followed by

$$MX_3OH + H_2O \rightleftharpoons MX_2(OH)_2 + HX, \quad (7)$$

$$MX_2(OH)_2 + H_2O \rightleftharpoons MX(OH)_3 + HX, \quad (8)$$

$$MX(OH)_3 + H_2O \rightleftharpoons M(OH)_4 + HX, \quad (9)$$

$$M(OH)_4 + M(OH)_4 \rightleftharpoons M(OH)_3\text{–}O\text{–}M(OH)_3 \text{ (condensation)}. \quad (10)$$

Stages (7)–(10) can also be concluded with chain growth, cyclization, and formation of condensed reaction products, including fine crystalline MO_2.

The hydroxy derivatives formed in stages (3) or (6)–(9) can undergo further transformations up to the formation of MO_2:

$$MX_3OH \rightleftharpoons X_2M = O + H_2O, \quad (11)$$

$$M(OH)_4 \rightleftharpoons (HO)_2M{=}O + H_2O, \quad (12)$$

$$MX_2(OH)_2 \rightleftharpoons X_2M{=}O + H_2O, \quad (13)$$

$$(HO)_2M{=}O \rightleftharpoons MO_2 + H_2O. \quad (14)$$

It should be noted that the case of low H_2O/MX_4 ratios (traces of water in MX_4) is typical for refining of MX_4, and reactions (3)–(6) show the state of the water impurity in purified compounds. At the same time, this case is also of interest as intermediate in consideration of the overall hydrolysis reaction.

A direct experimental estimation of the thermodynamic parameters of these reactions by a thermochemical method is almost impossible due to the difficulty of isolating most participating compounds in pure form in the standard crystalline state. Therefore, estimation of these parameters by quantum-chemistry methods is of interest. Previously, quantum-chemical calculations were used for estimating the reactions of silicon fluorides and chlorides (see, e.g., [11, 12]); however, the series (M = C, Si, Ge; X = H, F, Cl) was not systematically studied in these works. In addition, earlier quantum-chemical calculations rank below the state-of-the-art methods in accuracy.

This study deals with calculation, by one of the modern high-precision quantum-chemical methods, of standard thermodynamic functions (enthalpy, entropy, and Gibbs free energy) of individual reactions of the overall hydrolysis of MX_4 compounds, namely, reactions (3)–(4), (7)–(9), and (11)–(14). Unfortunately, calculation of more complicated processes (for example, (6) and (10)) is beyond the capability of the method.

COMPUTATIONAL METHOD

The thermodynamic parameters of individual compounds involved in the above reaction were calculated by the G3 method [13] of the family of Gx extrapolation methods. The error of these methods in calculation of enthalpies of formation is estimated at 5–10 kJ mol^{-1} [14]. The estimates of entropy contributions and Gibbs energy are considerably less accurate since entropy is considered in the rigid rotator–harmonic oscillator approximation, which can lead to noticeable errors (on the order of few J K^{-1} mol^{-1} per rotor) if high-amplitude oscillations and/or internal rotations (especially complicated by the existence of several asymmetric rotors as in molecules of polyhydroxy derivatives) occur in a molecule. However, analysis of the results demonstrates that, in most reactions under consideration, characteristic errors of the harmonic approximation are, as rule, considerably smaller than the difference in Gibbs energy between the reactions to be compared. In the case of germanium derivatives, calculation by the G3 method is impossible since it lacks the basis set of atomic orbitals for the germanium atom. Therefore, for calculation of the reactions of germanium derivatives, the G2 method [15] was used. This method, a predecessor of G3, is characterized by a somewhat higher mean error. For the Ge_2F_6O and Ge_2Cl_6O compounds, calculation by this method was impossible because of computational difficulties. The thermodynamic parameters of these compounds were calculated by the simpler G2MP2 method [16], which ranks slightly below the G2 method in accuracy. Calculations were performed with the GAUSSIAN 98 program package [17]. In all cases, quantum-chemical calculation provides accurate energies and thermodynamic functions of individual compounds in the ideal gas state with respect to the state of isolated nuclei and electrons, which can be reduced to the enthalpies (entropies) of formation from some standard state. The choice of the standard state for quantum-chemical estimation of thermochemical parameters is always difficult since it is impossible to accurately estimate systems in the condensed state. Therefore, in this study, we calculated the changes in the functions of formation of individual compounds, rather than these functions per se, in the course of reactions (3)–(4), (7)–(9), and (11)–(14). This approach eliminates the need to discuss the standard state and makes it possible to directly compare reactions. The tables summarize the data pertaining to the pressure $p = 1$ atm and temperature 298.15 K, unless otherwise specified.

RESULTS AND DISCUSSION

The results of calculations of standard thermodynamic functions of reactions (3)–(4), (7)–(9), and (11)–(14) at 298 K are summarized in Tables 1–3, and those for reactions (3), (7), (4), and (12) are shown as plots in Figs. 1–4.

Table 1. Calculated thermodynamic parameters (kJ mol^{-1}) of partial hydrolysis reactions of CX_4 molecules (X = H, F, Cl)

Reaction	$\Delta_r E$[a]	$\Delta_r H^0(0)$[b]	$\Delta_r H^0(298)$[c]	$\Delta_r G^0(298)$[c]	$\Delta_r S^0(298)$[c]
$CH_4 + H_2O = CH_3OH + H_2$	124.4	113.1	113.1	115.0	–6.4
$CH_3OH + CH_4 = C_2H_6O + H_2$	103.0	88.0	89.5	96.2	–22.5
$2CH_3OH = C_2H_6O + H_2O$	–21.4	–25.0	–23.6	–18.7	–16.4
$CH_3OH + H_2O = CH_2(OH)_2 + H_2$	74.0	59.4	60.2	68.9	–29.2
$CH_2(OH)_2 + H_2O = CH(OH)_3 + H_2$	33.9	14.5	12.8	30.6	–59.7
$CH(OH)_3 + H_2O = C(OH)_4 + H_2$	26.3	12.1	15.2	21.0	–19.5
$CH_3OH = CH_2O + H_2$	117.2	80.8	88.2	55.3	110.3
$C(OH)_4 = C(OH)_2O + H_2O$[d]	–16.8	–29.5	–24.5	–68.4	147.2
$CH_2(OH)_2 = CH_2O + H_2O$	43.1	21.3	27.9	–13.5	138.9
$C(OH)_2O = CO_2 + H_2O$[d]	–15.1	–33.3	–26.3	–67.6	138.5
$CF_4 + H_2O = CF_3OH + HF$	–9.2	–9.6	–9.5	–13.5	13.4
$CF_3OH + CF_4 = C_2F_6O + HF$	24.2	17.5	18.9	28.7	–32.9
$2CF_3OH = C_2F_6O + H_2O$	33.4	27.2	28.4	42.2	–46.3
$CF_3OH + H_2O = CF_2(OH)_2 + HF$	–8.1	–8.2	–8.2	–5.9	–7.7
$CF_2(OH)_2 + H_2O = CF(OH)_3 + HF$	–6.2	–6.0	–6.1	–0.6	–18.4
$CF(OH)_3 + H_2O = C(OH)_4 + HF$	–1.0	0.7	0.1	1.2	–4.0
$CF_3OH = CF_2O + HF$	39.3	24.5	30.1	–12.1	141.5
$CF_2(OH)_2 = CF_2O + H_2O$	47.5	32.8	38.4	–6.1	149.3
$CCl_4 + H_2O = CCl_3OH + HCl$	–25.2	–26.8	–28.1	–31.9	12.7
$CCl_3OH + CCl_4 = C_2Cl_6O + HCl$	7.5	–2.8	0.8	5.2	–14.8
$2CCl_3OH = C_2Cl_6O + H_2O$	32.8	24.0	28.8	37.1	–27.8
$CCl_3OH + H_2O = CCl_2(OH)_2 + HCl$	–31.3	–32.7	–33.8	–31.8	–6.7
$CCl_2(OH)_2 + H_2O = CCl(OH)_3 + HCl$	–35.5	–36.6	–37.6	–32.6	–16.8
$CCl(OH)_3 + H_2O = C(OH)_4 + HCl$	–29.2	–29.4	–28.5	–121.1	310.7
$CCl_3OH = CCl_2O + HCl$	–23.1	–39.0	–34.7	–78.0	145.2
$CCl_2(OH)_2 = CCl_2O + H_2O$	8.2	–6.3	–0.9	–46.2	151.9

[a] The change in the electron–nuclear energy in the course of reaction calculated by the quantum-chemical methods used in this work.

[b] Standard enthalpy of reaction at 0 K.

[c] Standard enthalpy, Gibbs energy, and entropy of reaction at 298 K.

[d] An analogous reaction occurs in the case of CF_4 and CCl_4

As is seen, at the early stage of hydrolysis (3), the $\Delta_r H^0(298)$ and $\Delta_r G^0(298)$ values considerably depend on both M and X (Fig. 1). On going from X = H to X = Cl at the carbon atom, these values become more negative; the strongest change is observed when H is changed for F. Upon the same change of substituents at the germanium atom, a weak opposite dependence is observed. The silicon derivatives occupy an intermediate position. Reaction (3) of silane hydrolysis is the most thermodynamically favorable one. For the second stage of hydrolysis, reaction (4) of formation of a compound with an M–O–M bond, the trend in the thermodynamic functions is somewhat different (Fig. 2). For methane, they become negative, whereas, for CF_4 and CCl_4, they have close positive values. Reaction (4) is clearly thermodynamically allowed for the silicon derivatives and basically allowed for the two calculated germanium derivatives. For reaction (7) of secondary hydrolysis, the trend in $\Delta_r H^0(298)$ and $\Delta_r G^0(298)$ in Fig. 3 is analogous to that in Fig. 1. However, in all cases, reaction (7) is thermodynamically forbidden. Again, large negative values of the silane thermodynamic functions are noteworthy. For reaction (13) of the concluding stage of hydrolysis, the changes in standard thermodynamic functions are shown in Fig. 4. The formation of products with a double bond M=O is thermodynamically allowed only for the carbon derivatives and is almost impossible under standard conditions for the germanium and especially silicon derivatives.

Thus, the dependences of the standard thermodynamic functions of the separate stages of hydrolysis of

Table 2. Calculated thermodynamic parameters (kJ mol^{-1}) of partial hydrolysis reactions of SiX_4 molecules (X = H, F, Cl)

Reaction	$\Delta_r E^{a}$	$\Delta_r H^0(0)^{b}$	$\Delta_r H^0(298)^{c}$	$\Delta_r G^0(298)^{c}$	$\Delta_r S^0(298)^{c}$
$SiH_4 + H_2O = SiH_3OH + H_2$	–63.6	–74.3	–73.3	–72.0	–4.4
$SiH_3OH + SiH_4 = Si_2H_6O + H_2$	–89.1	–101.4	–96.8	–103.9	23.8
$2SiH_3OH = Si_2H_6O + H_2O$	–25.4	–27.1	–23.4	–31.9	28.5
$SiH_3OH + H_2O = SiH_2(OH)_2 + H_2$	–93.4	–106.1	–104.2	–97.0	–24.1
$SiH_2(OH)_2 + H_2O = SiH(OH)_3 + H_2$	–110.3	–123.2	–121.6	–111.5	–33.9
$SiH(OH)_3 + H_2O = Si(OH)_4 + H_2$	–107.2	–120.4	–118.8	–107.7	–37.2
$SiH_3OH = SiH_2O + H_2^{d}$	197.9	173.6	180.1	148.5	106.0
$Si(OH)_4 = Si(OH)_2O + H_2O$	291.9	284.0	287.4	246.6	136.8
$SiH_2(OH)_2 = SiH_2O + H_2O$	291.3	279.7	284.3	245.5	130.1
$Si(OH)_2O = SiO_2 + H_2O^{d}$	297.5	286.1	291.9	252.3	132.8
$SiF_4 + H_2O = SiF_3OH + HF$	31.9	28.3	29.2	22.7	21.8
$SiF_3OH + SiF_4 = Si_2F_6O + HF$	12.2	7.4	11.8	6.8	16.8
$2SiF_3OH = Si_2F_6O + H_2O$	–19.7	–20.9	–17.4	–15.9	–5.0
$SiF_3OH + H_2O = SiF_2(OH)_2 + HF$	35.2	32.3	32.9	33.9	–3.4
$SiF_2(OH)_2 + H_2O = SiF(OH)_3 + HF$	38.0	34.6	35.6	34.7	3.0
$SiF(OH)_3 + H_2O = Si(OH)_4 + HF$	39.1	39.9	38.3	46.8	–28.5
$SiF_3OH = SiF_2O + HF$	382.0	371.3	375.1	336.8	128.5
$SiF_2(OH)_2 = SiF_2O + H_2O$	346.8	338.9	342.2	302.9	131.8
$SiCl_4 + H_2O = SiCl_3OH + HCl$	–14.9	–21.0	–21.4	–27.0	18.8
$SiCl_3OH + SiCL_4 = Si_2Cl_6O + HCl$	–39.9	–48.4	–44.5	–47.0	8.4
$2SiCl_3OH = Si_2Cl_6O + H_2O$	–24.9	–27.3	–23.0	–19.9	–10.4
$SiCl_3OH + H_2O = SiCl_2(OH)_2 + HCl$	–16.1	–22.8	–25.0	–20.5	–15.1
$SiCl_2(OH)_2 + H_2O = SiCl(OH)_3 + HCl$	–16.6	–21.5	–20.1	–20.9	2.7
$SiCl(OH)_3 + H_2O = Si(OH)_4 + HCl$	–12.2	–15.3	–17.2	–14.5	–9.1
$SiCl_3OH = SiCl_2O + HCl$	294.9	281.2	284.1	244.1	134.2
$SiCl_2(OH)_2 = SiCl_2O + H_2O$	311.1	304.0	309.1	264.6	149.3

[a–c] See notes to Table 1.

[d] Analogous reactions occur in the case of SiF_4 and $SiCl_4$.

Table 3. Calculated thermodynamic parameters (kJ mol^{-1}) of partial hydrolysis reactions of GeX_4 molecules (X = H, F, Cl)

Reaction	$\Delta_r E^a$	$\Delta_r H^0(0)^b$	$\Delta_r H^0(298)^c$	$\Delta_r G^0(298)^c$	$\Delta_r S^0(298)^c$
$GeH_4 + H_2O = GeH_3OH + H_2$	–4.1	–15.3	–16.3	–9.8	–21.8
$GeH_3OH + GeH_4 = Ge_2H_6O + H_2$	–5.6	–19.9	–19.4	4.2	–79.2
$2GeH_3OH = Ge_2H_6O + H_2O$	–1.5	–4.7	–3.0	14.0	–57.1
$GeH_3OH + H_2O = GeH_2(OH)_2 + H_2$	–31.9	–43.3	–39.3	–32.6	–22.5
$GeH_2(OH)_2 + H_2O = GeH(OH)_3 + H_2$	–36.0	–49.9	–46.8	–37.6	–30.9
$GeH(OH)_3 + H_2O = Ge(OH)_4 + H_2$	–36.8	–49.5	–47.4	–39.7	–25.8
$GeH_3OH = GeH_2O + H_2^d$	217.2	193.4	202.3	168.7	112.7
$Ge(OH)_4 = Ge(OH)_2O + H_2O$	142.2	132.7	136.3	93.3	144.2
$GeH_2(OH)_2 = GeH_2O + H_2O$	120.7	108.2	113.0	72.7	135.2
$Ge(OH)_2O = GeO_2 + H_2O^d$	55.3	46.9	51.3	16.2	117.7
$GeF_4 + H_2O = GeF_3OH + HF$	5.9	2.7	3.7	–3.4	23.8
$GeF_3OH + GeF_4 = Ge_2F_6O + HF$	5.8	1.0	5.3	0.3	16.8
$2GeF_3OH = Ge_2F_6O + H_2O$	–0.1	–1.7	1.6	3.8	–7.4
$GeF_3OH + H_2O = GeF_2(OH)_2 + HF$	8.9	6.5	7.0	8.7	–5.7
$GeF_2(OH)_2 + H_2O = GeF(OH)_3 + HF$	12.6	9.1	10.4	5.5	16.4
$GeF(OH)_3 + H_2O = Ge(OH)_4 + HF$	14.9	15.6	14.0	25.5	–38.6
$GeF_3OH = GeF_2O + HF$	171.5	161.2	164.4	127.8	122.8
$GeF_2(OH)_2 = GeF_2O + H_2O$	165.4	157.6	160.3	122.1	128.1
$GeCl_4 + H_2O = GeCl_3OH + HCl$	32.9	26.6	26.3	23.6	9.1
$GeCl_3OH + GeCl_4 = Ge_2Cl_6O + HCl$	12.0	2.4	1.7	14.3	–42.0
$2GeCl_3OH = Ge_2Cl_6O + H_2O$	–22.9	–26.2	–26.5	–11.4	–51.0
$GeCl_3OH + H_2O = GeCl_2(OH)_2 + HCl$	31.9	25.8	25.5	25.4	0.3
$GeCl_2(OH)_2 + H_2O = GeCl(OH)_3 + HCl$	32.7	26.6	26.3	26.4	–0.3
$GeCl(OH)_3 + H_2O = Ge(OH)_4 + HCl$	31.1	27.0	25.3	30.7	–18.1
$GeCl_3OH = GeCl_2O + HCl$	293.9	280.1	282.5	243.7	130.1
$GeCl_2(OH)_2 = GeCl_2O + H_2O$	262.0	254.3	256.9	218.2	129.8

[a–c] See notes to Table 1.

[d] Analogous reactions occur in the case of GeF_4 and $GeCl_4$.

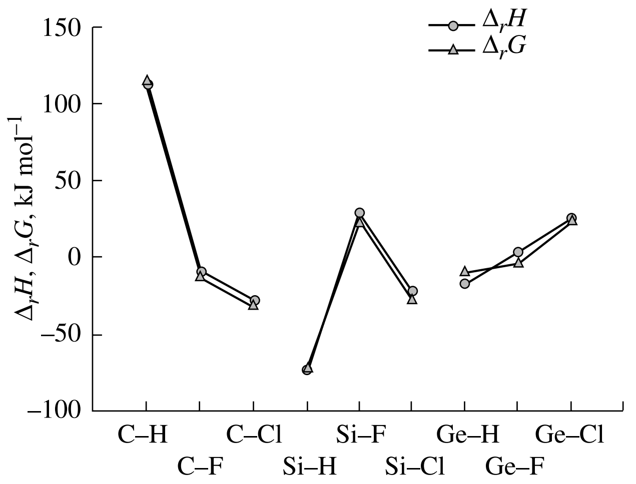

Fig. 1. Change in the thermodynamic parameters $\Delta_rH^0(298)$ and $\Delta_rG^0(298)$ of the reaction $MX_4 + H_2O \rightleftarrows MX_3OH + HX$ for various MX_4.

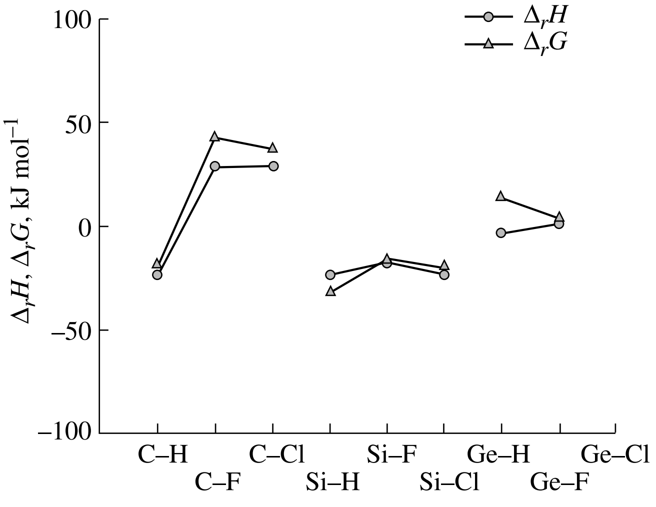

Fig. 2. Change in the thermodynamic parameters $\Delta_rH^0(298)$ and $\Delta_rG^0(298)$ of the reaction $2MX_3OH = MX_3OMX_3 + H_2O$ for various MX_3OH.

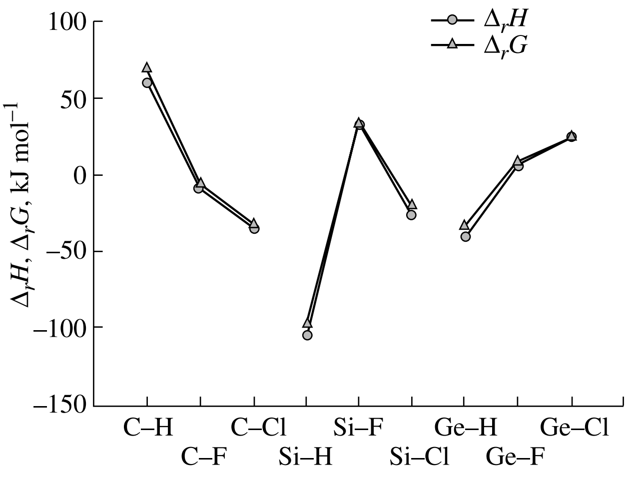

Fig. 3. Change in the thermodynamic parameters $\Delta_rH^0(298)$ and $\Delta_rG^0(298)$ of the reaction $MX_3OH + H_2O = MX_2(OH)_2 + HX$ for various MX_3OH.

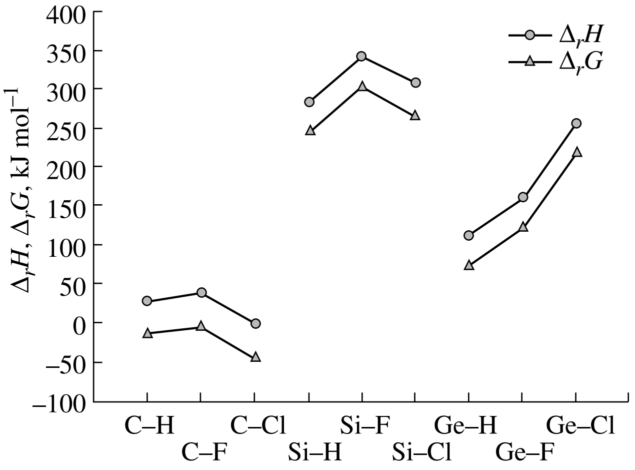

Fig. 4. Change in the thermodynamic parameters $\Delta_rH^0(298)$ and $\Delta_rG^0(298)$ of the reaction $M(OH)_4 = M(OH)_2O + H_2O$ for various MX_4.

MX_4 molecules on the nature of M and X have a complex character, which is likely explained by the bond energy balance in molecules, both the products and initial compounds. This problem calls for further study.

The formation of the products of reactions (3) and (4) was experimentally observed for $SiCl_4$ and $GeCl_4$ in an inert solvent and in molten chlorides [18–22] and for SiF_4 and GeF_4 in the gas phase [23, 24]. For SiF_4, the calculated $\Delta_rG^0(298)$ values of reactions (3) and (4) are in good agreement with the experimentally determined values.

Table 4 presents the $\Delta_rH^0(298)$ and $\Delta_rG^0(298)$ values of the overall reactions of hydrolysis (1) or (2) for all the compounds under consideration calculated from the standard thermodynamic functions of formation of the initial molecules and reaction products (both experimental and calculated) taken from [25] and obtained by summation of the corresponding values for reactions (3)–(14). As is seen, the results of both approaches are in agreement.

Thus, the standard thermodynamic functions of various stages of the hydrolysis of MX_4 molecules (M = C, Si, Ge; X = H, F, Cl) were determined using the G3 high-precision quantum-chemical method and its modifications for calculation of thermodynamic parameters. It was revealed which reactions are thermodynamically

Table 4. Calculated thermodynamic parameters (kJ mol^{-1}) of complete hydrolysis reactions of MX_4 molecules in comparison with the values obtained from tabulated values of standard thermodynamic functions of formation of the reaction participants [25] (parenthesized)

Reaction	$\Delta_r E^a$	$\Delta_r H^0(0)^b$	$\Delta_r H^0(298)^c$	$\Delta_r G^0(298)^c$
$CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g)$	226.8	136.4	150.6 (164)	99.7 (113)
$CF_4(g) + 2H_2O(g) = CO_2(g) + 4HF(g)$	–56.6	–86.3	–74.9 (–82.2)	–155.0 (–161.0)
$CCl_4(g) + 2H_2O(g) = CO_2(g) + 4HCl(g)$	–153.3	–188.3	–181.3 (–184)	–262.7 (–265)
$SiH_4(g) + 2H_2O(g) = SiO_2(g) + 4H_2(g)$	214.8	146.0	161.3 (127)	110.6 (104)
$SiF_4(g) + 2H_2O(g) = SiO_2(g) + 4HF(g)$	733.8	705.5	715.6 (684)	637.3 (605)
$SiCl_4(g) + 2H_2O(g) = SiO_2(g) + 4HCl(g)$	529.4	489.3	495.4 (454)	415.9 (374)
$GeH_4(g) + 2H_2O(g) = GeO_2(g) + 4H_2(g)$	351.2	284.1	300.1 (286)	252.1 (313)
$GeF_4(g) + 2H_2O(g) = GeO_2(g) + 4HF(g)$	502.6	476.3	485.4 (474)	408.3 (397)
$GeCl_4(g) + 2H_2O(g) = GeO_2(g) + 4HCl(g)$	588.9	548.4	553.6 (508)	478.4 (490.5)

[a–c] See notes to Table 1.

preferable for each type of molecule. The resulting values of standard thermodynamic functions can be used for estimating the theoretical limits of the contents of water and hydrolysis products in high-purity compounds of Group IVA elements.

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