CALCULATION OF THERMODYNAMIC FUNCTIONS OF HALOGEN DERIVATIVES OF SILANE AND GERMANE

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Molar heat capacity, absolute entropy, relative enthalpy and relative Gibbs energy were calculated for all halogen derivatives of silane and germane. The calculation was performed for the ideal gas state at atmospheric pressure in the temperature range 100 to 1 500 K in the usual rigid rotator — harmonic oscillator approximation. In the case of molecules where the necessary experimental values of fundamental vibrational frequencies were missing, the calculation was performed using the predicted frequencies. On the basis of the values of molar heat capacities obtained in both these ways, a critical examination of the influence of the inaccuracy of the predicted vibration frequencies on the accuracy of calculated ideal gas thermodynamic functions was made.

Tetrahedral molecules of the type AXYZV, where the central atom A is silicon or germanium and the substituent atoms X, Y, Z, or V are halogens and/or hydrogen, are of great importance in the chemistry of silicon and germanium compounds. The values of thermodynamic functions of compounds belonging to the above-mentioned group have been published so far only in such cases when the experimental vibrational spectrum of the molecule in question was available.

In a preceding paper[1], a modified Urey–Bradley force field was used for predicting the wavenumbers of the fundamental vibrations of halogen derivatives of silane and germane on the basis of the vibrational spectra of the molecules of the type AX_4 and AX_2Y_2. The results of these predictions can also be used for calculating thermodynamic functions of the above-mentioned compounds in the same way as in the case of the halogen derivatives of methane[2].

The aim of this paper is the calculation of thermodynamic functions of the above-mentioned silane and germane derivatives in the ideal-gas state, *i.e.* of the relative molar enthalpy, molar heat capacity, relative molar Gibbs energy and absolute entropy.

Computational Method

Thermodynamic functions of the compounds in question have been calculated under the assumption that the molecules behave as rigid rotators and that all the molecular vibrations are harmonic. The calculation have been performed for the ideal-gas standard state at the pressure 101·325 kPa and in the temperature range 100 to 1 500 K. The principal moments of inertia were calculated under the assumption

of tetrahedral structure of all the molecules investigated and average values of internuclear distances were used; these average internuclear distances are summarized in Table I. The same assumption and the same average internuclear distances were used in a previous communication[1] when calculating the force constants and the wavenumbers of molecular vibrations.

TABLE I

Average values of internuclear distances r for silanes and germanes

Bond	Si–H	Si–F	Si–Cl	Si–Br	Si–I
r, pm	148	156	202	217	243
Bond	Ge–H	Ge–F	Ge–Cl	Ge–Br	Ge–I
r, pm	153	167	209	232	248

TABLE II

Comparison of molar heat capacities calculated on the basis of experimental and of predicted wavenumbers of fundamental vibrations

Substance	Average difference $J\,K^{-1}\,mol^{-1}$	Maximum difference $J\,K^{-1}\,mol^{-1}$	Temperature K	Ref.[a]
SiH_3F	0·369	0·654	400	4
$SiHF_3$	0·374	0·747	400	5
SiH_3Cl	0·067	0·151	300	4
$SiHCl_3$	0·286	0·64	400	6
SiH_3Br	0·239	0·543	900	4
$SiHBr_3$	0·238	0·579	100	6
SiH_3I	0·252	0·656	300	7
$SiHI_3$	0·378	0·676	100	6
SiF_3Cl	0·681	1·456	400	8
$SiFCl_3$	0·248	0·50	300	8
SiF_3Br	0·582	1·236	400	9
$SiFBr_3$	0·378	0·66	300	9
$SiFI_3$	0·417	0·833	100	10
$SiCl_3Br$	0·085	0·385	100	11
$SiClBr_3$	0·185	0·45	300	12
$SiCl_3I$	0·109	0·26	300	11
$SiClI_3$	0·087	0·25	200	11
$SiBr_2I$	0·073	0·348	100	6

TABLE II
(*Continued*)

Substance	Average difference $J\,K^{-1}\,mol^{-1}$	Maximum difference $J\,K^{-1}\,mol^{-1}$	Temperature K	Ref.[a]
$SiBrI_3$	0·062	0·53	100	6
GeH_3F	0·148	0·216	100	13
GeH_3Cl	0·031	0·119	150	13
$GeHCl_3$	0·155	0·265	100	13
GeH_3Br	0·09	0·193	300	13
$GeHBr_3$	0·314	0·57	300	14
GeH_3I	0·204	0·475	300	13
$GeCl_3Br$	0·025	0·075	100	15
$GeClBr_3$	0·061	0·379	100	15
$GeCl_3I$	0·059	0·223	100	16
SiH_2F_2	0·357	0·669	500	17
SiH_2Cl_2	0·127	0·229	250	18
SiH_2Br_2	0·128	0·236	200	11
SiF_2Cl_2	0·299	0·592	250	19
SiF_2Br_2	0·301	0·657	298	9
SiF_2I_2	0·396	0·695	200	20
$SiCl_2Br_2$	0·071	0·549	100	12
$SiCl_2I_2$	0·205	0·484	200	15
$SiBr_2I_2$	0·082	0·35	100	6
GeH_2F_2	0·43	0·981	200	21, 22
GeH_2Cl_2	0·045	0·177	150	22, 23
GeH_2Br_2	0·042	0·094	300	21, 24
GeH_2I_2	0·069	0·221	100	21, 25
$GeCl_2Br_2$	0·213	0·598	150	15
SiF_2BrI	0·172	0·365	250	20
$SiCl_2HI$	0·13	0·265	150	6
$SiCl_2FBr$	0·082	0·156	500	20
$SiCl_2FI$	0·063	0·14	300	20
$SiBr_2HI$	0·23	0·528	400	6
$SiBr_2FCl$	0·141	0·28	300	20
$SiBr_2FI$	0·167	0·301	500	20
SiI_2HCl	0·287	1·296	100	6
SiI_2HBr	0·153	0·344	150	6
SiI_2FCl	0·372	0·766	300	20
SiI_2FBr	0·28	0·565	298	20
$GeCl_2HBr$	0·255	0·529	298	14
$GeBr_2HCl$	0·442	0·909	250	14
$SiFClBrI$	0·261	0·908	100	20

[a] Experimental vibrational spectrum.

TABLE III

Values of relative enthalpy, $(H^0 - H_0^0)/T$, of the derivatives of silane ($JK^{-1} mol^{-1}$)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_4	25·055	37·617	− 5·495	0·97
SiF_4	30·583	77·696	−26·622	1·15
$SiCl_4$	43·948	78·041	−29·748	1·68
$SiBr_4$	56·641	66·031	−25·845	1·49
SiI_4	65·600	56·371	−22·464	1·30
SiH_3F	26·867	31·958	− 6·832	0·48
$SiHF_3$	29·209	43·462	−13·246	0·51
SiH_3Cl	27·391	35·169	− 8·762	0·25
$SiHCl_3$	34·573	45·702	−15·670	1·02
SiH_3Br	28·109	35·906	− 9·300	0·21
$SiHBr_3$	39·343	42·001	−14·659	1·03
SiH_3I	35·883	32·408	− 9·137	0·46
$SiHI_3$	43·053	38·721	−13·632	0·98
SiF_3Cl	33·108	53·456	−18·991	1·08
$SiFCl_3$	36·773	52·690	−19·410	1·25
SiF_3Br	33·854	53·375	−19·133	1·13
$SiFBr_3$	42·523	47·923	−18·029	1·22
SiF_3I	35·838	50·858	−18·203	1·08
$SiFI_3$	47·026	43·192	−16·388	1·11
$SiCl_3Br$	40·950	52·224	−20·078	1·43
$SiClBr_3$	44·957	48·467	−18·866	1·37
$SiCl_3I$	42·466	50·692	−19·556	1·40
$SiClI_3$	49·459	43·386	−17·024	1·23
$SiBr_3I$	49·021	44·449	−17·524	1·29
$SiBrI_3$	51·648	41·418	−16·404	1·21
SiH_2F_2	24·644	58·285	−15·692	0·41
SiH_2Cl_2	27·876	63·382	−19·219	0·68
SiH_2Br_2	31·199	62·769	−19·627	0·81
SiH_2I_2	33·826	60·350	−18·839	0·79
SiF_2Cl_2	36·909	79·055	−28·759	1·49
SiF_2Br_2	41·959	75·292	−27·791	1·49
SiF_2I_2	45·783	71·791	−26·688	1·44
$SiCl_2Br_2$	49·454	73·442	−28·411	1·64
$SiCl_2I_2$	53·586	69·436	−27·095	1·57
$SiBr_2I_2$	60·585	62·177	−24·595	1·43
SiH_2FCl	26·029	60·804	−17·382	0·41
SiH_2FBr	27·369	60·591	−17·562	0·48
SiH_2FI	26·810	59·685	−16·882	0·38
SiH_2ClBr	29·312	62·903	−19·241	0·72
SiH_2ClI	28·651	62·201	−18·670	0·61

TABLE III
(*Continued*)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_2BrI	32·424	61·367	−19·078	0·77
SiF_2HCl	29·323	69·208	−22·225	0·85
SiF_2HBr	31·022	68·871	−22·421	0·91
SiF_2HI	32·549	67·690	−22·100	0·92
SiF_2ClBr	38·146	75·921	−27·258	1·33
SiF_2ClI	41·406	74·970	−27·481	1·44
SiF_2BrI	43·583	73·776	−27·318	1·47
$SiCl_2HF$	32·031	71·014	−23·807	1·08
$SiCl_2HBr$	37·228	69·937	−24·345	1·25
$SiCl_2HI$	38·596	69·247	−24·258	1·26
$SiCl_2FBr$	42·654	77·138	−28·965	1·60
$SiCl_2FI$	44·672	75·137	−28·302	1·57
$SiCl_2BrI$	52·115	70·658	−27·443	1·58
$SiBr_2HF$	36·402	67·760	−22·964	1·10
$SiBr_2HCl$	39·542	68·181	−23·894	1·25
$SiBr_2HI$	43·874	65·327	−23·231	1·26
$SiBr_2FCl$	45·572	74·629	−28·220	1·58
$SiBr_2FI$	50·594	69·962	−26·737	1·51
$SiBr_2ClI$	55·415	67·275	−26·285	1·52
SiI_2HF	32·635	69·431	−23·046	1·01
SiI_2HCl	42·689	66·048	−23·383	1·25
SiI_2HBr	45·555	63·758	−22·720	1·24
SiI_2FCl	49·864	70·462	−26·845	1·50
SiI_2FBr	52·925	67·657	−25·970	1·47
SiI_2ClBr	57·347	65·586	−25·785	1·50
$SiHFClBr$	30·988	72·072	−24·187	1·12
$SiHFClI$	31·820	71·654	−24·144	1·14
$SiHFBrI$	32·982	71·035	−24·052	1·16
$SiHClBrI$	36·966	71·505	−25·177	1·36
$SiFClBrI$	47·841	72·485	−27·519	1·54

Where the experimentally determined vibrational spectra of the respective molecules were available, the calculations of the vibrational contributions to the thermodynamic functions were performed using the experimental values of the wavenumbers of fundamentals; when the experimental data were lacking, the wavenumbers given in the preceding paper[1] were used.

The wavenumbers of some of the fundamentals, especially in the case of totally

TABLE IV

Values of relative Gibbs energy, $(G^0 - H_0^0)/T$, of the derivatives of silane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_4	−135·258	−115·435	27·786	0·55
SiF_4	−180·916	−177·015	46·244	0·48
$SiCl_4$	−203·389	−221·787	62·567	0·61
$SiBr_4$	−234·280	−249·972	73·753	0·70
SiI_4	−259·801	−268·406	81·074	0·74
SiH_3F	−165·391	−116·348	30·808	0·51
$SiHF_3$	−189·619	−136·741	37·227	0·48
SiH_3Cl	−174·139	−121·758	32·661	0·49
$SiHCl_3$	−208·684	−157·179	44·505	0·52
SiH_3Br	−183·800	−125·053	33·775	0·48
$SiHBr_3$	−231·367	−168·778	49·119	0·54
SiH_3I	−194·122	−146·982	42·168	0·58
$SiHI_3$	−248·579	−177·238	52·495	0·56
SiF_3Cl	−201·183	−160·385	44·766	0·51
$SiFCl_3$	−212·234	−171·739	49·049	0·53
SiF_3Br	−208·558	−162·834	45·739	0·50
$SiFBr_3$	−233·476	−185·342	54·408	0·57
SiF_3I	−215·016	−166·529	47·239	0·52
$SiFI_3$	−250·819	−194·848	58·202	0·59
$SiCl_3Br$	−233·228	−185·097	54·000	0·57
$SiClBr_3$	−236·639	−194·069	57·441	0·59
$SiCl_3I$	−229·076	−188·392	55·392	0·57
$SiClI_3$	−253·561	−203·041	61·077	0·61
$SiBr_3I$	−248·255	−202·885	61·072	0·62
$SiBrI_3$	−258·679	−208·050	63·116	0·63
SiH_2F_2	−181·098	−136·185	33·303	0·41
SiH_2Cl_2	−196·447	−152·837	39·010	0·43
SiH_2Br_2	−214·087	−163·234	42·929	0·45
SiH_2I_2	−227·777	−169·134	45·211	0·46
SiF_2Cl_2	−207·014	−199·568	54·413	0·52
SiF_2Br_2	−222·858	−212·013	59·240	0·56
SiF_2I_2	−235·744	−220·674	62·605	0·58
$SiCl_2Br_2$	−232·849	−234·677	67·600	0·62
$SiCl_2I_2$	−239·335	−243·850	71·214	0·66
$SiBr_2I_2$	−260·349	−258·566	77·074	0·69
SiH_2FCl	−194·378	−143·754	35·922	0·40
SiH_2FBr	−203·383	−148·006	37·499	0·41
SiH_2FI	−210·684	−144·978	36·368	0·39
SiH_2ClBr	−210·884	−157·112	40·689	0·43
SiH_2ClI	−218·013	−153·951	39·488	0·41

TABLE IV
(*Continued*)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_2BrI	−226·545	−165·594	43·907	0·44
SiF_2HCl	−202·631	−163·702	42·222	0·44
SiF_2HBr	−210·866	−169·001	44·293	0·45
SiF_2HI	−217·609	−172·741	45·679	0·46
SiF_2ClBr	−221·251	−199·947	54·745	0·51
SiF_2ClI	−227·349	−209·809	58·463	0·54
SiF_2BrI	−234·724	−215·642	60·713	0·55
$SiCl_2HF$	−210·074	−174·767	46·141	0·46
$SiCl_2HBr$	−223·793	−190·774	52·190	0·50
$SiCl_2HI$	−230·091	−194·514	53·571	0·51
$SiCl_2FBr$	−225·998	−216·444	60·670	0·56
$SiCl_2FI$	−232·564	−220·829	62·529	0·57
$SiCl_2BrI$	−245·485	−240·288	69·904	0·63
$SiBr_2HF$	−227·315	−185·609	50·402	0·49
$SiBr_2HCl$	−232·347	−196·451	54·403	0·52
$SiBr_2HI$	−246·362	−207·472	58·686	0·54
$SiBr_2FCl$	−234·684	−223·212	63·420	0·57
$SiBr_2FI$	−248·243	−234·477	67·790	0·61
$SiBr_2ClI$	−253·692	−247·323	72·617	0·65
SiI_2HF	−237·021	−174·900	46·413	0·43
SiI_2HCl	−245·519	−204·399	57·408	0·53
SiI_2HBr	−253·122	−211·234	60·055	0·55
SiI_2FCl	−248·380	−232·585	67·040	0·60
SiI_2FBr	−255·516	−239·575	69·774	0·62
SiI_2ClBr	−259·437	−251·820	74·350	0·66
$SiHFClBr$	−215·511	−172·629	45·396	0·44
$SiHFClI$	−221·564	−174·923	46·271	0·44
$SiHFBrI$	−228·894	−178·039	47·440	0·44
$SiHClBrI$	−234·262	−191·754	52·500	0·48
$SiFClBrI$	−239·985	−228·243	65·366	0·59

halogenated germanes, are very low. The dimensionless quantity x, *i.e.* the argument in the Einstein functions appearing in the vibrational contributions to the thermodynamic functions, $x = hc\tilde{\nu}/kT$, can therefore attain low values and the accuracy of the following calculations is lowered. Therefore, the standard formulas of statistical thermodynamics[3] were modified in such a way that for $x < 0{\cdot}1$ the function $1 - e^{-x}$ was calculated using the Taylor's series expansion.

TABLE V

Values of absolute entropy, S^0, of the derivatives of silane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_4	160·227	153·082	— 33·455	0·26
SiF_4	211·471	254·714	— 72·861	0·61
$SiCl_4$	247·308	299·842	— 92·347	0·82
$SiBr_4$	291·080	315·960	— 99·456	0·86
SiI_4	325·550	324·910	— 103·457	0·85
SiH_3F	192·269	148·318	— 37·705	0·35
$SiHF_3$	218·823	180·221	— 50·418	0·48
SiH_3Cl	201·645	156·978	— 41·401	0·41
$SiHCl_3$	243·233	202·952	— 60·284	0·60
SiH_3Br	211·949	161·008	— 43·070	0·42
$SiHBr_3$	270·562	210·833	— 63·779	0·62
SiH_3I	229·982	179·420	— 51·234	0·56
$SiHI_3$	291·444	215·998	— 65·969	0·62
SiF_3Cl	234·103	213·928	— 63·811	0·60
$SiFCl_3$	248·870	224·481	— 68·480	0·65
SiF_3Br	242·276	216·265	— 64·806	0·61
$SiFBr_3$	275·760	233·275	— 72·280	0·68
SiF_3I	250·836	217·490	— 65·398	0·61
$SiFI_3$	297·554	238·061	— 74·427	0·68
$SiCl_3Br$	264·087	237·327	— 74·030	0·71
$SiClBr_3$	281·414	242·558	— 76·226	0·72
$SiCl_3I$	271·383	239·085	— 74·769	0·71
$SiClI_3$	303·026	246·499	— 78·144	0·71
$SiBr_3I$	297·189	247·323	— 78·514	0·73
$SiBrI_3$	310·412	249·438	— 79·509	0·72
SiH_2F_2	205·817	194·537	— 49·011	0·34
SiH_2Cl_2	224·374	216·265	— 58·267	0·46
SiH_2Br_2	245·131	226·061	— 62·588	0·51
SiH_2I_2	261·443	229·557	— 64·186	0·52
SiF_2Cl_2	243·843	278·625	— 83·167	0·70
SiF_2Br_2	264·817	287·285	— 86·933	0·73
SiF_2I_2	281·414	292·473	— 89·287	0·73
$SiCl_2Br_2$	282·325	308·190	— 96·054	0·82
$SiCl_2I_2$	293·086	313·333	— 98·380	0·83
$SiBr_2I_2$	320·990	320·792	— 101·696	0·83
SiH_2FCl	220·384	204·666	— 53·245	0·39
SiH_2FBr	230·763	208·651	— 55·115	0·41
SiH_2FI	237·494	204·666	— 53·272	0·37
SiH_2ClBr	240·133	220·006	— 59·849	0·47
SiH_2ClI	246·431	216·221	— 58·158	0·43
SiH_2BrI	258·889	227·041	— 62·817	0·50

TABLE V
(*Continued*)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiF_2HCl	231·886	232·985	— 64·529	0·51
SiF_2HBr	241·786	237·994	— 66·697	0·53
SiF_2HI	250·135	240·510	— 67·779	0·54
SiF_2ClBr	259·163	275·886	— 81·938	0·66
SiF_2ClI	268·829	284·814	— 85·922	0·71
SiF_2BrI	278·313	289·489	— 87·906	0·72
$SiCl_2HF$	241·974	245·764	— 70·100	0·57
$SiCl_2HBr$	260·896	260·747	— 76·487	0·63
$SiCl_2HI$	268·556	263·775	— 77·807	0·64
$SiCl_2FBr$	268·647	293·563	— 89·515	0·75
$SiCl_2FI$	277·310	295·968	— 90·695	0·75
$SiCl_2BrI$	297·737	310·996	— 97·141	0·81
$SiBr_2HF$	263·631	253·401	— 73·350	0·59
$SiBr_2HCl$	271·839	264·644	— 78·182	0·65
$SiBr_2HI$	290·168	272·836	— 81·830	0·67
$SiBr_2FCl$	280·319	297·927	— 91·564	0·76
$SiBr_2FI$	298·922	304·562	— 94·575	0·77
$SiBr_2ClI$	309·227	314·691	— 99·005	0·81
SiI_2HF	269·376	244·429	— 69·323	0·52
SiI_2HCl	288·253	270·499	— 80·628	0·66
SiI_2HBr	298·831	275·085	— 82·743	0·67
SiI_2FCl	298·375	303·137	— 93·940	0·76
SiI_2FBr	308·679	307·300	— 95·820	0·78
SiI_2ClBr	316·795	317·474	— 100·158	0·81
$SiHFClBr$	246·402	244·718	— 69·540	0·56
$SiHFClI$	253·327	246·588	— 70·258	0·56
$SiHFBrI$	261·808	249·148	— 71·524	0·56
$SiHClBrI$	271·109	263·352	— 77·443	0·64
$SiFClBrI$	287·797	300·799	— 92·782	0·77

RESULTS AND DISCUSSION

The temperature dependence of thermodynamic functions of individual substances was expressed as a quadratic function of temperature, *e.g.*

$$C_{pm} = A + BT + CT^2 \qquad (1)$$

TABLE VI

Values of the molar heat capacity, C^0_{pm}, of the derivatives of silane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %	Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
SiH_4	16·163	101·490	−32·813	0·70	SiH_2FCl	29·791	105·293	−39·874	1·00
SiF_4	47·214	98·426	−41·178	1·31	SiH_2FBr	32·492	101·054	−38·102	1·87
$SiCl_4$	72·120	64·341	−28·525	1·00	SiH_2FI	29·791	105·529	−39·950	1·95
$SiBr_4$	84·454	43·169	−19·366	1·39	SiH_2ClBr	37·810	94·911	−36·172	1·98
SiI_4	91·646	30·501	−13·806	1·01	SiH_2ClI	35·103	99·507	−38·113	1·11
SiH_3F	22·837	74·152	−26·253	1·15	SiH_2BrI	42·443	87·662	−33·178	1·76
$SiHF_3$	34·316	67·885	−26·291	1·70	SiF_2HCl	40·494	98·799	−39·341	1·13
SiH_3Cl	26·816	69·589	−24·856	1·28	SiF_2HBr	43·561	94·300	−37·542	1·02
$SiHCl_3$	46·615	51·336	−20·187	1·56	SiF_2HI	45·476	91·029	−36·134	1·90
SiH_3Br	28·970	66·875	−23·834	1·19	SiF_2ClBr	59·222	81·662	−34·846	1·07
$SiHBr_3$	52·417	41·606	−16·018	1·18	SiF_2ClI	65·007	72·623	−31·156	1·89
SiH_3I	41·064	47·653	−15·975	0·69	SiF_2BrI	68·153	67·591	−29·074	1·77
$SiHI_3$	56·128	35·627	−13·469	0·94	$SiCl_2HF$	46·963	90·783	−36·591	1·14
SiF_3Cl	46·507	61·506	−26·318	1·04	$SiCl_2HBr$	55·717	78·144	−31·715	1·94
$SiFCl_3$	53·113	51·467	−22·290	1·82	$SiCl_2HI$	57·473	75·673	−30·753	1·90
SiF_3Br	48·080	59·000	−25·269	1·97	$SiCl_2FBr$	69·196	67·658	−29·558	1·95
$SiFBr_3$	59·718	40·267	−17·469	1·40	$SiCl_2FI$	71·111	64·296	−28·090	1·84
SiF_3I	49·978	54·871	−23·274	1·71	$SiCl_2BrI$	80·578	49·825	−22·285	1·58
$SiFI_3$	63·537	33·598	−14·540	1·13	$SiBr_2HF$	52·634	81·150	−32·427	1·81
$SiCl_3Br$	60·568	40·779	−18·165	1·67	$SiBr_2HCl$	58·561	73·469	−29·704	1·80
$SiClBr_3$	64·660	33·695	−15·072	1·40	$SiBr_2HI$	63·771	65·499	−26·470	1·62
$SiCl_3I$	62·009	38·212	−17·034	1·56	$SiBr_2FCl$	72·479	62·092	−27·166	1·78
$SiClI_3$	68·022	27·616	−12·382	1·14	$SiBr_2FI$	77·461	53·588	−23·481	1·54
$SiBr_3I$	68·461	27·051	−12·181	1·15	$SiBr_2ClI$	83·473	44·771	−20·073	1·43
$SiBrI_3$	70·251	23·804	−10·746	1·01	SiI_2HF	46·798	90·339	−36·200	1·01
SiH_2F_2	24·804	111·450	−41·961	1·96	SiI_2HCl	62·249	67·903	−27·454	1·68
SiH_2Cl_2	35·325	98·789	−37·792	1·13	SiI_2HBr	65·384	62·760	−25·296	1·54
SiH_2Br_2	41·469	89·468	−34·042	1·90	SiI_2FCl	76·446	55·280	−24·209	1·58
SiH_2I_2	44·307	84·474	−31·819	1·66	SiI_2FBr	79·661	49·714	−21·807	1·42
SiF_2Cl_2	60·163	81·016	−34·830	1·17	SiI_2ClBr	85·685	40·942	−18·372	1·32
SiF_2Br_2	66·501	70·441	−30·302	1·86	$SiHFClBr$	46·399	91·421	−36·803	1·15
SiF_2I_2	70·393	63·807	−27·449	1·66	$SiHFClI$	47·681	89·407	−35·960	1·09
$SiCl_2Br_2$	78·361	53·766	−23·975	1·70	$SiHFBrI$	49·414	86·664	−34·819	1·00
$SiCl_2I_2$	82·379	46·753	−20·910	1·49	$SiHClBrI$	57·108	76·296	−31·014	1·94
$SiBr_2I_2$	88·261	36·512	−16·469	1·20	$SiFClBrI$	74·691	58·241	−25·497	1·66

TABLE VII

Values of relative enthalpy, $(H^0 - H_0^0)/T$, of the derivatives of germane ($J\ K^{-1}\ mol^{-1}$)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %	Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_4	24·678	41·790	− 7·485	0·75	GeH_2FCl	28·184	64·804	−19·980	0·75
GeF_4	36·790	78·656	−28·465	1·41	GeH_2FBr	30·019	63·534	−19·687	0·77
$GeCl_4$	50·514	74·338	−29·183	1·75	GeH_2FI	31·261	62·433	−19·350	0·75
$GeBr_4$	63·503	60·757	−24·503	1·50	GeH_2ClBr	32·367	63·897	−20·421	0·93
GeI_4	72·018	50·293	−20·497	1·25	GeH_2ClI	33·706	62·725	−20·057	0·92
GeH_3F	26·850	36·388	− 9·186	0·30	GeH_2BrI	36·033	60·883	−19·562	0·93
$GeHF_3$	32·298	44·734	−14·545	0·74	GeF_2HCl	33·843	71·707	−24·535	1·17
GeH_3Cl	28·127	37·672	−10·245	0·28	GeF_2HBr	36·020	69·934	−24·030	1·17
$GeHCl_3$	37·673	44·796	−15·752	1·12	GeF_2HI	37·434	68·596	−23·584	1·15
GeH_3Br	29·500	37·107	−10·224	0·34	GeF_2ClBr	46·051	74·838	−28·460	1·16
$GeHBr_3$	43·492	39·229	−13·985	1·05	GeF_2ClI	47·601	73·121	−27·829	1·57
GeH_3I	30·446	36·682	−10·186	0·36	GeF_2BrI	50·394	70·371	−26·921	1·53
$GeHI_3$	47·174	34·647	−12·246	0·92	$GeCl_2HF$	36·670	71·322	−24·954	1·30
GeF_3Cl	36·681	53·085	−19·584	1·25	$GeCl_2HBr$	42·597	68·814	−24·899	1·43
$GeFCl_3$	40·711	51·359	−19·529	1·36	$GeCl_2HI$	43·999	66·569	−23·954	1·36
GeF_3Br	38·625	51·530	−19·154	1·26	$GeCl_2FBr$	49·482	73·580	−28·530	1·68
$GeFBr_3$	46·792	45·231	−17·464	1·25	$GeCl_2FI$	51·335	71·519	−27·786	1·64
GeF_3I	39·822	50·215	−18·692	1·23	$GeCl_2BrI$	58·476	66·333	−26·497	1·62
$GeFI_3$	51·215	39·858	−15·447	1·09	$GeBr_2HF$	43·048	67·724	−24·416	1·41
$GeCl_3Br$	45·379	49·456	−19·546	1·49	$GeBr_2HCl$	45·795	65·606	−23·807	1·38
$GeClBr_3$	49·494	45·046	−17·991	1·39	$GeBr_2HI$	50·035	60·467	−21·883	1·25
$GeCl_3I$	47·054	47·540	−18·861	1·43	$GeBr_2FCl$	49·750	62·924	−23·182	1·40
$GeClI_3$	53·449	40·162	−16·132	1·23	$GeBr_2FI$	57·513	65·009	−25·546	1·51
$GeBr_3I$	53·780	40·349	−16·344	1·28	$GeBr_2ClI$	62·739	61·491	−24·720	1·52
$GeBrI_3$	56·327	37·188	−15·094	1·18	GeI_2HF	44·928	63·257	−22·290	1·18
GeH_2F_2	25·499	65·212	−19·595	0·62	GeI_2HCl	48·473	61·904	−22·332	1·27
GeH_2Cl_2	30·292	66·025	−21·149	0·96	GeI_2HBr	51·523	58·776	−21·274	1·21
GeH_2Br_2	32·310	63·022	−19·883	0·82	GeI_2FCl	55·472	67·033	−26·209	1·54
GeH_2I_2	37·109	61·183	−19·915	1·00	GeI_2FBr	59·371	62·742	−24·677	1·46
GeF_2Cl_2	43·099	77·301	−29·161	1·62	GeI_2ClBr	63·993	59·977	−24·187	1·48
GeF_2Br_2	48·325	72·427	−27·601	1·57	$GeHFClBr$	36·659	71·990	−25·372	1·37
GeF_2I_2	52·058	68·127	−26·030	1·46	$GeHFClI$	37·753	71·000	−25·035	1·36
$GeCl_2Br_2$	56·663	68·337	−27·209	1·66	$GeHFBrI$	40·289	68·920	−24·432	1·35
$GeCl_2I_2$	60·602	63·428	−25·307	1·53	$GeHClBrI$	43·954	67·422	−24·432	1·43
$GeBr_2I_2$	67·099	56·504	−22·916	1·41	$GeClBrI$	51·050	72·324	−28·188	1·68

TABLE VIII

Values of relative Gibbs energy, $(G^0 - H_0^0)/T$, of the derivatives of germane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_4	−146·304	−118·708	28·568	0·50
GeF_4	−187·487	−198·588	53·957	0·55
$GeCl_4$	−209·772	−239·353	69·421	0·68
$GeBr_4$	−241·199	−266·781	80·237	0·76
GeI_4	−265·820	−282·788	86·662	0·80
GeH_3F	−175·194	−121·201	32·183	0·48
$GeHF_3$	−196·846	−148·318	41·434	0·51
GeH_3Cl	−183·424	−127·057	34·433	0·48
$GeHCl_3$	−214·337	−166·240	48·081	0·55
GeH_3Br	−193·158	−131·019	35·917	0·49
$GeHBr_3$	−237·243	−179·331	53·169	0·58
GeH_3I	−199·422	−133·691	36·944	0·49
$GeHI_3$	−252·934	−186·299	55·925	0·60
GeF_3Cl	−206·997	−171·873	49·022	0·55
$GeFCl_3$	−217·626	−183·316	53·441	0·57
GeF_3Br	−214·594	−176·503	50·897	0·55
$GeFBr_3$	−239·227	−196·384	58·624	0·61
GeF_3I	−220·179	−179·019	51·891	0·56
$GeFI_3$	−254·946	−204·867	62·039	0·63
$GeCl_3Br$	−228·346	−196·718	58·430	0·61
$GeClBr_3$	−242·150	−205·223	61·914	0·63
$GeCl_3I$	−233·807	−200·080	59·865	0·62
$GeClI_3$	−257·037	−212·637	64·855	0·65
$GeBr_3I$	−253·509	−214·017	65·431	0·66
$GeBrI_3$	−263·079	−216·737	67·295	0·67
GeH_2F_2	−189·163	−146·849	36·689	0·40
GeH_2Cl_2	−203·543	−163·969	43·005	0·45
GeH_2Br_2	−221·758	−167·064	44·206	0·45
GeH_2I_2	−232·433	−180·956	49·505	0·50
GeF_2Cl_2	−213·568	−218·113	61·354	0·59
GeF_2Br_2	−229·471	−229·757	65·975	0·62
GeF_2I_2	−241·535	−237·238	68·948	0·64
$GeCl_2Br_2$	−239·700	−252·866	74·758	0·69
$GeCl_2I_2$	−251·868	−260·169	77·612	0·71
$GeBr_2I_2$	−266·458	−273·682	83·112	0·75
GeH_2FCl	−202·181	−155·398	39·743	0·42
GeH_2FBr	−211·328	−160·006	41·624	0·44
GeH_2FI	−217·290	−162·989	42·804	0·44
GeH_2ClBr	−218·264	−168·377	44·668	0·46
GeH_2ClI	−224·277	−171·405	45·885	0·46

TABLE VIII
(*Continued*)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_2BrI	−233·322	−177·082	48·060	0·48
GeF_2HCl	−208·940	−181·468	48·657	0·48
GeF_2HBr	−217·409	−186·655	50·630	0·50
GeF_2HI	−223·228	−189·839	51·891	0·51
GeF_2ClBr	−226·944	−225·104	64·121	0·59
GeF_2ClI	−232·632	−228·365	65·344	0·60
GeF_2BrI	−240·771	−234·366	67·763	0·62
$GeCl_2HF$	−216·218	−190·462	51·989	0·51
$GeCl_2HBr$	−229·407	−207·382	58·370	0·56
$GeCl_2HI$	−235·146	−209·431	59·191	0·57
$GeCl_2FBr$	−232·211	−235·078	67·823	0·62
$GeCl_2FI$	−237·830	−238·774	69·437	0·67
$GeCl_2BrI$	−250·682	−256·606	76·247	0·69
$GeBr_2HF$	−233·425	−207·650	58·561	0·56
$GeBr_2HCl$	−238·839	−214·217	61·121	0·58
$GeBr_2HI$	−252·136	−222·343	64·279	0·61
$GeBr_2FCl$	−242·088	−224·436	64·942	0·62
$GeBr_2FI$	−253·874	−251·864	74·530	0·67
$GeBr_2ClI$	−260·166	−265·111	79·590	0·71
GeI_2HF	−245·918	−208·607	59·072	0·56
GeI_2HCl	−250·466	−218·804	62·942	0·59
GeI_2HBr	−258·029	−225·393	65·659	0·61
GeI_2FCl	−252·506	−247·345	72·698	0·65
GeI_2FBr	−260·257	−255·338	76·003	0·68
GeI_2ClBr	−265·090	−267·493	80·596	0·72
$GeHFClBr$	−221·450	−191·353	52·261	0·50
$GeHFClI$	−226·870	−193·824	53·261	0·50
$GeHFBrI$	−234·422	−199·835	55·674	0·52
$GeHClBrI$	−239·791	−210·343	59·517	0·56
$GeClBrI$	−242·544	−238·885	69·434	0·62

This type of function proved to be sufficiently accurate in the temperature range from 200 to 1 500 K. The constants of the correlation equation (*1*) evaluated by the least squares treatment of calculated data, together with the average error of the correlation (in per cent) are given in Tables III–X.

The error caused by the use of the estimated frequencies of the fundamental molecular vibrations represents the main source of inaccuracy in the above mentioned calculations. To examine the influence of this error, the molar heat capacity was

TABLE IX

Values of absolute entropy, S^0, of the derivatives of germane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_4	170·959	160·474	— 36·102	0·28
GeF_4	224·254	277·267	— 82·514	0·72
$GeCl_4$	260·166	313·756	— 98·413	0·90
$GeBr_4$	304·667	327·537	— 104·767	0·90
GeI_4	337·860	333·081	— 107·289	0·88
GeH_3F	201·975	157·646	— 41·526	0·39
$GeHF_3$	229·065	193·112	— 55·946	0·55
GeH_3Cl	211·596	164·815	— 44·673	0·44
$GeHCl_3$	251·942	211·034	— 63·768	0·64
GeH_3Br	222·704	168·132	— 46·038	0·46
$GeHBr_3$	280·410	218·625	— 67·056	0·66
GeH_3I	229·726	170·359	— 47·141	0·47
$GeHI_3$	299·743	220·896	— 68·078	0·65
GeF_3Cl	243·496	224·970	— 68·665	0·66
$GeFCl_3$	258·251	234·633	— 72·888	0·71
GeF_3Br	253·059	228·043	— 70·058	0·67
$GeFBr_3$	285·791	241·668	— 75·905	0·72
GeF_3I	259·853	229·245	— 70·513	0·67
$GeFI_3$	306·217	244·740	— 77·503	0·71
$GeCl_3Br$	273·662	246·187	— 77·932	0·76
$GeClBr_3$	291·536	250·328	— 79·726	0·76
$GeCl_3I$	280·593	247·657	— 78·552	0·76
$GeClI_3$	310·686	252·800	— 81·063	0·75
$GeBr_3I$	307·321	254·492	— 81·618	0·77
$GeBrI_3$	319·622	255·872	— 82·411	0·76
GeH_2F_2	214·531	212·102	— 56·332	0·43
GeH_2Cl_2	233·789	230·002	— 63·996	0·54
GeH_2Br_2	254·051	230·180	— 64·186	0·51
GeH_2I_2	269·285	242·113	— 69·113	0·58
GeF_2Cl_2	256·519	295·456	— 90·401	0·78
GeF_2Br_2	277·857	302·358	— 93·412	0·80
GeF_2I_2	293·724	305·385	— 95·032	0·79
$GeCl_2Br_2$	296·369	321·215	— 101·902	0·88
$GeCl_2I_2$	312·783	323·619	— 102·941	0·87
$GeBr_2I_2$	333·483	330·209	— 105·816	0·78
GeH_2FCl	230·461	220·273	— 59·854	0·47
GeH_2FBr	241·096	223·635	— 61·331	0·49
GeH_2FI	248·631	225·505	— 62·208	0·49
GeH_2ClBr	250·557	232·295	— 65·002	0·54
GeH_2ClI	257·886	234·165	— 65·860	0·54

TABLE IX
(*Continued*)

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_2BrI	269·285	237·972	— 67·589	0·56
GeF_2HCl	242·549	253·267	— 73·013	0·61
GeF_2HBr	253·327	256·718	— 74·660	0·62
GeF_2HI	260·622	258·454	— 75·371	0·62
GeF_2ClBr	273·115	300·020	— 92·260	0·79
GeF_2ClI	280·319	301·356	— 93·005	0·79
GeF_2BrI	291·353	304·784	— 94·619	0·79
$GeCl_2HF$	252·780	261·883	— 76·726	0·65
$GeCl_2HBr$	271·930	276·243	— 83·221	0·72
$GeCl_2HI$	279·134	275·998	— 83·080	0·71
$GeCl_2FBr$	281·687	308·725	— 96·315	0·82
$GeCl_2FI$	289·256	310·372	— 97·065	0·82
$GeCl_2BrI$	309·044	322·929	— 102·712	0·86
$GeBr_2HF$	276·489	275·508	— 82·911	0·71
$GeBr_2HCl$	284·605	279·961	— 84·732	0·73
$GeBr_2HI$	302·296	282·899	— 86·200	0·72
$GeBr_2FCl$	291·992	287·374	— 88·129	0·76
$GeBr_2FI$	311·506	316·918	— 100·022	0·83
$GeBr_2ClI$	322·996	326·669	— 104·368	0·86
GeI_2HF	290·806	271·879	— 81·226	0·67
GeI_2HCl	299·013	280·762	— 85·308	0·71
GeI_2HBr	309·774	284·191	— 86·835	0·72
GeI_2FCl	308·041	314·447	— 98·897	0·82
GeI_2FBr	319·713	318·165	— 100·658	0·82
GeI_2ClBr	329·015	327·560	— 104·653	0·86
$GeHFClBr$	258·069	263·397	— 77·563	0·66
$GeHFClI$	264·543	264·866	— 78·106	0·66
$GeHFBrI$	274·666	268·829	— 79·949	0·67
$GeHClBrI$	283·876	277·801	— 83·890	0·72
$GeClBrI$	293·633	311·285	— 97·489	0·82

chosen because the corresponding expression derived from statistical thermodynamics contains the second derivative of the partition function with respect to the temperature; therefore, it can be expected that the changes of the frequencies will have the greatest influence on the value of the molar heat capacity. The values of C_{pm} in the temperature range 100–1 500 K were calculated for the compounds for which the experimental values of the fundamental wavenumbers were available; at the same time, these calculations were repeated using the calculated wavenumbers. The results of these calculations are compared in Table II.

TABLE X

Values of the molar heat capacity, C^0_{pm}, of the derivatives of germane (J K^{-1} mol^{-1})

Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %	Substance	A	$B \cdot 10^3$	$C \cdot 10^6$	Average error, %
GeH_4	17·543	103·655	−34·569	0·83	GeH_2FCl	36·841	97·887	−37·678	1·11
GeF_4	58·806	83·866	−36·129	1·25	GeH_2FBr	39·491	93·296	−35·656	1·92
$GeCl_4$	81·895	48·245	−21·747	1·62	GeH_2FI	40·927	90·843	−34·607	1·81
$GeBr_4$	93·561	27·317	−12·447	0·95	GeH_2ClBr	44·604	85·835	−32·754	1·81
GeI_4	98·662	17·833	− 8·180	0·62	GeH_2ClI	46·034	83·372	−31·705	1·71
GeH_3F	25·847	72·962	−26·601	1·46	GeH_2BrI	48·867	78·641	−29·650	1·54
$GeHF_3$	40·756	60·222	−23·655	1·65	GeF_2HCl	50·423	87·049	−35·444	1·15
GeH_3Cl	30·156	66·557	−24·068	1·34	GeF_2HBr	53·210	82·151	−33·292	1·96
$GeHCl_3$	51·676	43·881	−17·159	1·32	GeF_2HI	54·623	79·725	−32·221	1·86
GeH_3Br	32·583	62·538	−22·334	1·17	GeF_2ClBr	73·722	60·222	−26·421	1·75
$GeHBr_3$	57·695	33·435	−12·577	0·85	GeF_2ClI	75·021	57·907	−25·378	1·66
GeH_3I	34·008	60·391	−21·470	1·10	GeF_2BrI	77·842	52·831	−23·138	1·48
$GeHI_3$	60·106	28·703	−10·414	0·61	$GeCl_2HF$	55·866	78·678	−32·052	1·98
GeF_3Cl	53·022	52·072	−22·655	1·87	$GeCl_2HBr$	65·230	64·051	−26·068	1·65
$GeFCl_3$	59·382	42·058	−18·535	1·62	$GeCl_2HI$	65·703	62·693	−25·345	1·55
GeF_3Br	55·581	47·563	−20·665	1·68	$GeCl_2FBr$	79·410	51·394	−22·801	1·58
$GeFBr_3$	65·309	31·408	−13·800	1·16	$GeCl_2FI$	80·886	48·623	−21·573	1 48
GeF_3I	56·652	45·604	−19·774	1·58	$GeCl_2BrI$	89·657	34·285	−15·551	1·16
$GeFI_3$	68·193	26·049	−11·393	0·91	$GeBr_2HF$	65·583	62·560	−25·247	1·52
$GeCl_3Br$	67·071	29·802	−13·474	1·31	$GeBr_2HCl$	68·262	58·664	−23·676	1·45
$GeClBr_3$	70·621	23·372	−10·599	1·03	$GeBr_2HI$	71·339	52·697	−20·932	1·20
$GeCl_3I$	68·387	27·366	−12·371	1·20	$GeBr_2FCl$	73·887	49·269	−19·633	1·12
$GeClI_3$	73·015	18·875	− 8·572	0·82	$GeBr_2FI$	86·494	38·560	−17·072	1·15
$GeBr_3I$	74·257	16·759	− 7·664	0·76	$GeBr_2ClI$	92·860	28·475	−12·947	0·97
$GeBrI_3$	75·631	14·176	− 6·495	0·64	GeI_2HF	64·073	64·185	−25·655	1·43
GeH_2F_2	31·438	106·485	−41·233	1·38	GeI_2HCl	69·612	55·725	−22·274	1·29
GeH_2Cl_2	42·461	89·821	−34·574	1·01	GeI_2HBr	72·456	50·738	−20·062	1·13
GeH_2Br_2	42·916	88·812	−34·053	1·90	GeI_2FCl	84·425	42·233	−18·719	1·26
GeH_2I_2	51·107	75·741	−28·590	1·49	GeI_2FBr	87·668	36·334	−16·105	1·07
GeF_2Cl_2	70·211	66·300	−29·090	1·93	GeI_2ClBr	93·732	26·872	−12·219	0·92
GeF_2Br_2	75·859	56·259	−24·639	1·59	$GeHFClBr$	57·034	76·608	−31·183	1·93
GeF_2I_2	78·696	51·072	−22·285	1·40	$GeHFClI$	58·122	74·871	−30·405	1·85
$GeCl_2Br_2$	88·158	37·046	−16·784	1·26	$GeHFBrI$	61·217	69·550	−28·090	1·64
$GeCl_2I_2$	90·398	32·838	−14·877	1·10	$GeHClBrI$	66·979	60·512	−24·416	1·49
$GeBr_2I_2$	96·023	22·753	−10·398	0·79	$GeClBrI$	81·519	47·599	−21·144	1·46

As can be seen from the data in Table II, the error in the value of the molar heat capacity caused by the uncertainty of the predicted fundamental wavenumbers is generally small. In Table II, the values of the molar heat capacity calculated in both the before-mentioned ways are compared for 56 compounds; only in the case of two of them the maximum difference between both heat-capacity values amounted to 2–3%, with nine compounds the difference was between 1–2% and in the case of remaining 45 substances it was less than 1%.

This result can be considered as satisfactory with regard to the fact that the prediction of thermodynamic functions by this method does not require any experimental data for the given molecule. The before-mentioned errors are comparable with the errors of contemporary contribution methods used for the estimation of thermodynamic functions. Our estimation method can be used especially in the case of simple molecules where the assumption of transferability of force constants is applicable and where the respective contributions necessary when using other methods for estimating thermodynamic functions are often not available.

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