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Ideal Gas Thermodynamic Properties of Selected Bromoethanes and Iodoethane

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The available molecular parameters, fundamental frequencies, potential barrier heights, torsional frequencies, and standard enthalpies of formation at 298.15 K for selected bromoethanes and iodoethane containing one symmetric-top group have been critically evaluated and recommended values selected. The chemical thermodynamic properties in the ideal gas state at one atmosphere pressure using the rigid-rotor harmonic-oscillator approximation have been calculated for CH_3CH_2Br, CH_3CHBr_2, CH_3CBr_3, C_2Br_6, and CH_3CH_2I. The internal rotational contributions have been obtained from the partition function formed by the summation of internal rotation energy levels.

Key words: Bromoethanes; iodoethane; ideal gas thermodynamic properties; internal rotation; potential barrier heights; torsional frequencies; symmetric top.

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1. Introduction

This work involves the calculation of the ideal gas thermodynamic properties of bromoethanes and iodoethane in which at least one of the groups is a symmetric top. The literature survey complete up to 1976 revealed that the vibrational frequencies were available for only CH_3CH_2Br, CH_3CHBr_2, CH_3CBr_3, C_2Br_6, and CH_3CH_2I. For these molecules, molecular parameters, potential barrier heights, and standard enthalpies of formation were estimated or derived when experimental values were not available.

The procedures for evaluation, selection, and calculation of these values, the physical constants and the atomic weights, are the same as those in references 1 and 2. The enthalpy and Gibbs energy functions of the elements in their reference states, tabulated in [1][1] were used in the calculation of ΔH_f°, ΔG_f°, and $\log K_f$ for the compounds studied. (Please note that $H^\circ - H_0^\circ$ at 100 K for H_2 should be 759.9 cal mol^{-1} instead of 758.9 cal mol^{-1} in [1].)[2]

Using the selected values of the above parameters, the ideal gas thermodynamic properties: heat capacity (C_p°), entropy, (S°), enthalpy, ($H^\circ - H_0^\circ$), Gibbs energy function, $[-(G^\circ - H_0^\circ)/T]$, enthalpy of formation, (ΔH_f°), Gibbs energy of formation, (ΔG_f°), and the logarithm of the equilibrium constant of formation, ($\log K_f$) for the above compounds have been computed, assuming a rigid-rotor harmonic-oscillator approx-

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[1] Figures in brackets indicate literature references at the end of this paper.

[2] Energy values are given in calories to permit convenient use of these tables in conjunction with other thermodynamic tables (1 cal=4.184 J).

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imation, at a pressure of one atomosphere (101325 Pa) and at temperatures from 0-1500 K. The internal rotation contributions to the thermodynamic properties for each compound were calculated by the use of a partition function formed by the summation of the internal rotation energy levels according to the procedures discussed in reference 3. With our present computer program we could calculate energy levels up to 15000 cm^{-1}.[3]

1.1. Estimation of the Standard Enthalpies of Formation

The standard enthalpies of formation are available only for CH_3CH_2Br and CH_3CH_2I. In order to obtain ΔH_f°, ΔG_f°, and log K_f as a function of temperature it was necessary to have $\Delta H_f^\circ(298.15)$ for CH_3CHBr_2, CH_3CBr_3, and C_2Br_6. Hence we had to estimate these values. Recently Somayajulu and Zwolinski [4] have shown that using the triatomic additivity scheme, realistic values of $\Delta H_f^\circ(298)$ can be predicted for the substituted alkanes. According to them $\Delta H_f^\circ(298)$ can be written in terms of the Θ and Λ parameters as follows for the symmetric top bromoethanes:

$$\Delta H_f^\circ(CH_3CH_2Br) = \Theta(HHH)+4\Theta(HHC)+\Theta(HHBr) +2\Theta(HBrC)+2\Lambda(HBr)$$

$$\Delta H_f^\circ(CH_3CHBr_2) = \Theta(HHH)+3\Theta(HHC)+\Theta(HBrBr) +2\Theta(HBrC)+\Theta(BrBrC)+4\Lambda(HBr)$$

$$\Delta H_f^\circ(CH_3CBr_3) = \Theta(HHH)+3\Theta(HHC)+\Theta(BrBrBr) +3\Theta(BrBrC)+6\Lambda(HBr)$$

$$\Delta H_f^\circ(CH_2BrCBr_3) = \Theta(HHC)+\Theta(HHBr)+2\Theta(HBrC) +\Theta(BrBrBr)+3\Theta(BrBrC)+4\Lambda(HBr)$$

$$\Delta H_f^\circ(CHBr_2CBr_3) = \Theta(HBrBr)+2\Theta(HBrC)+\Theta(BrBrBr) +4\Theta(BrBrC)+2\Lambda(HBr)$$

$$\Delta H_f^\circ(C_2Br_6) = 2\Theta(BrBrBr)+6\Theta(BrBrC)$$

Using the following values [4] of the Θ parameters and $\Lambda(HBr)=-1.15$ (kcal mol^{-1})

$\Theta(HHH)=-4.470\pm0.005$ $\Theta(HBrC)=0.02\pm0.10$

$\Theta(HHC)=-1.883\pm0.005$ $\Theta(HBrBr)=1.7\pm1.0$

$\Theta(CCC)=0.052\pm0.005$ $\Theta(BrBrBr)=4.8\pm1.0$

$\Theta(HHBr)=-1.54\pm0.10$ $\Theta(BrBrC)=3.7\pm0.5$

($\Theta(BrBrC)=\frac{2}{3}(BrBrBr)+\frac{1}{3}(CCC)+0.5$ is assumed; 0.5 is the non-additivity correction). The estimated $\Delta H_f^\circ(298)$ values with uncertainties are (kcal mol^{-1}): CH_3CH_2Br: -15.8 ± 0.2; CH_3CHBr_2: -9.8 ± 1.1; CH_3CBr_3: -1.1 ± 1.8; CH_2BrCBr_3: 7.9 ± 1.8; $CHBr_2CBr_3$: 19.0 ± 2.5; CBr_3CBr_3: 31.8 ± 3.6. The estimated value for CH_3CH_2Br differs by 0.6 kcal mol^{-1} from the experimental value of -15.2 ± 0.5 kcal mol^{-1} but falls within its uncertainty limits. For CH_3CH_2Br we have selected $\Delta H_f^\circ(g, 298)=-15.2\pm0.5$ kcal mol^{-1}. While using the equilibrium constants of formation for bromoethanes one should keep in mind the large uncertainties present in these ΔH_f° values.

2. Bromoethane (CH_3CH_2Br)

The microwave spectrum has been investigated by Wagner, et al. [5] using two isotopic species and by Flanagan and Pierce [6] using ten isotopic species. We have adopted the values of molecular structure (table 1) and the moments of inertia obtained using the rotational constants of Flanagan and Pierce as they appear more reliable. Using their values of molecular parameters the reduced moments of intertia, I_r, have been calculated (table 2). Also, the moments calculated from the adopted structural parameters are reported in table 2 for comparison. For other references on the molecular parameters one is referred to reference [7].

Shimanouchi [8] has critically reviewed the infrared and Raman spectral data for bromoethane and assigned a complete set of vibrational frequencies. Since then some additional work has been carried out by other investigators.

Winther and Hummel [9] observed the combination band of the methyl torsion and the CH stretching frequencies of bromoethane in the infrared spectrum for the gaseous state and determined the CH stretching frequencies and the number of combination levels of the methyl group torsion. They concluded that the values for the symmetric CH stretching frequencies for *n*-alkyl compounds occur between 2940 and 2910 cm^{-1}.

Gaufres and Bejand-Bianchi [10] reported complete vibrational frequencies (except the torsional frequency) from their infrared and Raman spectral measurements in the liquid state and the normal coordinate analysis which agreed well with the values of Winther and Hummel. Recently, Suzuki et al. [11] reported a revised value of ν_{15} and the torsional frequency from their normal coordinate analysis of different isotopic species based upon the results of Gaufres and Bejand-Bianchi.

We have selected the values of Winther and Hummel and of Shimanouchi because they were measured for the gaseous state. ν_{15} and ν_{16} have been adopted from the work of Suzuki et al. and are presented in table 3.

The potential barrier height to the internal rotation of 3.684 kcal mol^{-1} has been reported by Flanagan and Pierce [6], based on the splitting of the rotational lines in the first excited torsional state reported by Lide [12]. Recently Durig et al. reported a value of 3.72 kcal mol^{-1} from the methyl torsional overtones in the Raman spectrum [13a] and from the far infrared measurements [13b], both in the gaseous state. They used the structural data of Flanagan and Pierce in their calculations. We have adopted an average of these above two values, namely, 3.70 kcal mol^{-1} in our calculations. This value corresponds to the torsional frequency $\nu_{18}=249$ cm^{-1}.

Cox and Pilcher [14] have critically evaluated the heats of reaction [15, 16, 17] for CH_3CH_2Br and recommended $\Delta H_f^\circ(CH_3CH_2Br, g, 298)=-15.2\pm0.5$ kcal mol^{-1}. This value is adopted here.

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[3] Vibrational energy levels and frequencies are given in terms of these wavenumber($\tilde{\nu}$) equivalents. The conversion to true energy units may be made through the relation $E=hc\tilde{\nu}$.

TABLE 1. Structural parameters for bromoethanes and iodoethane[a]

	CH_3CH_2Br	CH_3CHBr_2[b]	CH_3CBr_3	C_2Br_6	CH_3CH_2I
C-H(CH_3)	1.093	1.093	1.095		1.093
C-H(CH_2, CH)	1.087	1.087			1.087
C-C	1.518	1.52	1.525	1.526	1.54
C-Br(I)	1.95	1.95	1.927	1.944	2.14
HCH(CH_3)	108.9	109.0	109.0		109.5
HCH(CH_2)	109.9				109.5
CCBr(I)	111.0	111.0	107.3[d]		112.2
CCH(CH_2, CH)	112.2	112.2			109.5
HCBr	105.4				
BrCBr		113.0[c]	111.2	109.6	

[a] Bond length in angstroms (10^{-8} cm) and bond angles in degrees.
[b] Estimated values.
[c] Ref. [18].
[d] Durig, J.R., private communication.

TABLE 2. Molecular parameters for bromoethanes and iodoethane

	CH_3CH_2Br	CH_3CHBr_2[b]	CH_3CBr_3	C_2Br_6[b]	CH_3CH_2I
I_a (amu Å^2)	16.8781[a] 16.8123[b]	95.4151	476.221[c] 475.822[b]	1613.15	17.3633[d] 17.2574[c]
I_b (amu Å^2)	133.3000[a] 132.728[b]	430.937	476.221[c] 475.822[b]	1769.24	169.6358[d] 169.892[c]
I_c (amu Å^2)	143.9018[a] 143.160[b]	512.776	811.072[b]	1769.24	180.6796[d] 180.761[c]
I_r (amu Å^2)	2.8640	3.1694	3.1914	403.287	2.9105
F(cm^{-1})	5.8864	5.3194	5.2826	0.0418	5.7924
ν_τ (cm^{-1})	249	253	298[c]	51	245[c]
V_3 (kcal mol^{-1})	3.70	4.30	5.78	19.84[c]	3.66
σ(CH_3, CBr_3)	3	3	3	3	3
σ(overall)	1	1	3	6	1

[a] Ref. [6]; average of $CH_3CH_2{}^{79}Br$ and $CH_3CH_2{}^{81}Br$.
[b] Calculated from structural parameters.
[c] Ref. [21]; average of $CH_3C^{79}Br_3$, $CH_3C^{79}Br_2{}^{81}Br$, $CH_3C^{79}Br^{81}Br_2$ and $CH_3C^{81}Br_3$.
[d] Ref. [33].

The ideal gas thermodynamic properties were calculated using the data given in tables 1, 2, and 3 and are presented in table 4.

3. 1,1-Dibromoethane (CH_3CHBr_2)

Molecular parameters available for CH_3CHBr_2 are those reported by Morino et al. [18] from their electron-diffraction measurements in 1949. Their value for <CCBr=114° seemed rather high as compared to that in CH_3CH_2Br (111.0°) and in CH_3CBr_3 (107.7°). As Morino et al. used assumed values for most of the parameters we felt that better values could be estimated from more reliable data for CH_3CH_2Br and CH_3CBr_3. The estimated molecular parameters are given in table 1 and the calculated moments of inertia and the reduced moment of inertia are given in table 2.

Recently Durig et al. [19] reported for the first time, complete vibrational assignments from the infrared measurements in the gaseous state and the solid state and the Raman spectrum in the liquid and solid states. They carried out the normal coordinate analysis to confirm their assignments. We have adopted their gaseous state frequencies which are given in table 3.

The potential barrier height of 4.26 kcal mol^{-1} was reported by Durig et al. [19] from the torsional frequency (253 cm^{-1}) observed in the far infrared region. Durig et al. [20] also reported the value of 4.33 kcal mol^{-1} from the methyl torsional overtones in the Raman spectrum of the gaseous state.

TABLE 3. Vibrational frequencies for bromoethanes and iodoethane (cm^{-1})

	CH_3CH_2Br	CH_3CHBr_2^{b}	CH_3CBr_3	CBr_3CBr_3	CH_3CH_2I
ν_1	A' 2981	A' 3023	A_1 2943	A_g 940	A' 2986
ν_2	2959	2996	1378	255	2973
ν_3	2937	2937	1052	120	2932
ν_4	1465	1443	416	A_{1u} 51^{a}	1462
ν_5	1451	1383	230	A_{2u} 559	1429
ν_6	1386	1260	A_2 298^{a,b}	254	1385
ν_7	1252	1070	E 3004	E_g 768	1208
ν_8	1061	966	1440	204	1054
ν_9	964	545	1074	139	957
ν_{10}	583	342	639	E_u 656	509
ν_{11}	290	172	280	168	258
ν_{12}	A'' 3024	A'' 2985	152	82	A'' 3025
ν_{13}	2991	1443			2989
ν_{14}	1451	1172			1447
ν_{15}	1139	1045			1201
ν_{16}	1023	620			1049
ν_{17}	770	275			741
ν_{18}	249^{a}	253^{a}			245^{a,b}

^{a} Torsional frequency.

^{b} Calculated in this work.

TABLE 4. Ideal gas thermodynamic properties of CH_3CH_2Br

T	C°_p	S°	$-(G^\circ-H^\circ_0)/T$	$H^\circ-H^\circ_0$	ΔH°_f	ΔG°_f	$\log K_f$
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.00	0.00	0.00	0.00	−10.0	−10.0	Infinite
100	9.30	55.92	47.63	0.83	−11.4	−10.2	22.27
150	10.71	59.96	51.10	1.33	−11.9	−9.5	13.81
200	12.12	63.23	53.73	1.90	−12.6	−8.6	9.37
273.15	14.48	67.35	56.84	2.87	−14.8	−6.9	5.52
298.15	15.35	68.66	57.78	3.24	−15.2	−6.2	4.52
300	15.42	68.75	57.85	3.27	−15.2	−6.1	4.45
400	18.89	73.67	61.19	4.99	−19.8	−2.2	1.19
500	21.97	78.22	64.15	7.04	−20.6	2.4	−1.03
600	24.54	82.46	66.85	9.37	−21.3	7.0	−2.55
700	26.70	86.41	69.37	11.93	−21.7	11.8	−3.67
800	28.55	90.10	71.73	14.69	−22.1	16.6	−4.52
900	30.14	93.56	73.97	17.63	−22.4	21.4	−5.20
1000	31.53	96.81	76.09	20.72	−22.5	26.3	−5.75
1100	32.74	99.87	78.11	23.93	−22.6	31.2	−6.19
1200	33.79	102.76	80.05	27.26	−22.7	36.1	−6.57
1300	34.70	105.50	81.90	30.68	−22.7	41.0	−6.89
1400	35.50	108.11	83.68	34.20	−22.6	45.9	−7.17
1500	36.20	110.58	85.39	37.78	−22.5	50.8	−7.40

We have adopted the average value of 4.30 kcal mol^{-1} in this work.

No experimental ΔH°_f(298) is available for this compound. We have adopted the estimated value obtained by the procedure discussed in section 1.2.

The ideal gas thermodynamic properties were calculated using the data given in table 1, 2, and 3 and are presented in table 5.

4. 1,1,1-Tribromoethane (CH_3CBr_3)

Li et al. [21] reported for the first time the structural parameters from their microwave measurements of four isotopic species of CH_3CBr_3. They reported only one rotational constant. We have adopted their values to calculate the principal moments of inertia and the reduced moment of inertia which are given in table 2.

Stengle and Taylor [22] studied the Raman spectrum in the liquid state and reported all frequencies except the torsional frequency. Later, Durig et al. [23a] studied the infrared spectrum in the gaseous and solid states and found that the shifts between the liquid and gas values were relatively minor. They observed the torsional frequency (304 cm^{-1}) only for the solid state. Their vibrational frequencies for the gaseous state are adopted here and are reported in table 3. Recently, Durig et al. [20] observed the methyl torsional overtone in the Raman spectrum of the gaseous state, 2←0=583 cm^{-1} and 3←1=555 cm^{-1} and calculated a barrier height of

5.78 kcal mol^{-1}. We have adopted this value in our calculations. Ratcliffe and Waddington [23b] reported a similar value (5.62 kcal mol^{-1}) from the inelastic neutron scattering spectrum of solid CH_3CBr_3.

No experimental $\Delta H_f^\circ(298)$ is available for this compound and hence the estimated value discussed in section 1.2 is adopted here.

The ideal gas thermodynamic properties were calculated using the data given in table 1, 2, and 3 and are reported in table 6.

5. Hexabromoethane (C_2Br_6)

The molecular structure for the solid state is reported in the literature [24, 25]. We have adopted the values reported by Mandel and Donohue [25] as they used better techniques and the uncertainties in their values are small. These values are presented in table 1. The calculated moments of inertia and the reduced moment of inertia are given in table 2.

Shimanouchi [8] has critically reviewed the infrared and Raman spectrum and recommended the fundamental fre-

TABLE 5. Ideal gas thermodynamic properties of CH_3CHBr_2

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	log K_f
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.00	0.00	0.00	0.00	—3.3	—3.3	Infinite
100	10.94	62.42	53.60	0.88	—4.6	—4.7	10.17
150	13.35	67.33	57.38	1.49	—5.2	—4.5	6.63
200	15.37	71.45	60.40	2.21	—5.8	—4.2	4.64
273.15	18.10	76.65	64.07	3.44	—9.4	—3.4	2.74
298.15	19.02	78.27	65.19	3.90	—9.8	—2.9	2.10
300	19.08	78.39	65.28	3.93	—9.8	—2.8	2.05
400	22.52	84.36	69.32	6.02	—17.8	1.1	—0.62
500	25.42	89.71	72.87	8.42	—18.4	6.0	—2.60
600	27.76	94.56	76.09	11.08	—18.8	10.9	—3.95
700	29.66	98.99	79.05	13.96	—19.0	15.8	—4.94
800	31.24	103.05	81.80	17.01	—19.2	20.8	—5.68
900	32.58	106.81	84.37	20.20	—19.3	25.8	—6.27
1000	33.73	110.31	86.79	23.52	—19.3	30.8	—6.74
1100	34.72	113.57	89.08	26.94	—19.3	35.8	—7.12
1200	35.57	116.63	91.25	30.45	—19.3	40.8	—7.44
1300	36.32	119.51	93.31	34.05	—19.2	45.9	—7.71
1400	36.96	122.22	95.28	37.71	—19.0	50.9	—7.95
1500	37.52	124.79	97.16	41.44	—18.9	55.9	—8.14

TABLE 6. Ideal gas thermodynamic properties of CH_3CBr_3

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	log K_f
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.00	0.00	0.00	0.00	6.5	6.5	Infinite
100	13.44	64.72	54.98	0.97	5.3	4.4	—9.69
150	16.92	70.87	59.28	1.74	4.7	4.1	—6.02
200	19.48	76.10	62.85	2.65	4.1	4.0	—4.40
273.15	22.45	82.63	67.30	4.19	—0.6	4.3	—3.40
298.15	23.36	84.64	68.67	4.76	—1.1	4.7	—3.45
300	23.42	84.78	68.77	4.80	—1.1	4.7	—3.46
400	26.63	91.97	73.69	7.31	—12.4	9.0	—4.93
500	29.21	98.20	77.99	10.11	—12.7	14.4	—6.32
600	31.26	103.72	81.82	13.14	—12.8	19.9	—7.25
700	32.88	108.66	85.31	16.35	—12.9	25.4	—7.92
800	34.20	113.14	88.51	19.70	—12.8	30.8	—8.42
900	35.28	117.23	91.48	23.18	—12.8	36.3	—8.81
1000	36.19	121.00	94.25	26.75	—12.6	41.7	—9.12
1100	36.95	124.48	96.84	30.41	—12.4	47.1	—9.36
1200	37.60	127.73	99.28	34.14	—12.2	52.5	—9.57
1300	38.15	130.76	101.59	37.93	—12.0	57.9	—9.74
1400	38.63	133.61	103.77	41.77	—11.8	63.3	—9.89
1500	39.04	136.28	105.85	45.65	—11.6	68.7	—10.01

quencies for the solid state. McLachlan and Carter [26] studied the infrared and Raman spectra of oriented single crystals of C_2Br_6 and reported the vibrational assignments. Their values of ν_3, ν_4 (torsion), ν_6, and ν_{12} differed from those of Shimanouchi. They are given below (ν in cm^{-1}):

Assignment	McLachlan, Carter	Shimanouchi
ν_3	143	120
ν_4	65	51
ν_6	223	254
ν_{12}	108	82

McLachlan and Carter are doubtful about their value for the torsional frequency as it was picked to explain the various combination bands. Even Shimanouchi deduced his value from the combination band $(\nu_4+\nu_{10})$ and $(\nu_4+\nu_{11})$.

It was difficult to decide the reliability of these two sets of values. We felt that a comparison of the calculated value of the potential barrier with the values implied by these torsional frequency assignments would throw some light on the problem. The barrier is sufficiently high that it may be derived from the torsional frequency by a perturbed harmonic oscillator approximation. Hence we applied equation (1),

$$V_3(\text{cal mol}^{-1})=(\nu_\tau^2/9F+\nu_\tau/2+9F/4)2.859121, \qquad (1)$$

obtained by the procedure discussed by Allen et al. [28]. In equation (1), ν_τ is the torsional frequency, $F(\text{cm}^{-1})=h/8\pi^2cI_r$ where h is the Planck constant, c is the speed of light and I_r is the reduced moment of inertia.

The potential barrier heights derived from $\nu_\tau=65$ cm^{-1} and $\nu_\tau=51$ cm^{-1} are 32.2 and 19.84 kcal mol^{-1}, respectively. Mardashev et al. [29] have carried out simple quantum chemical calculations and obtained the rotational barrier heights for ethane and hexahaloethanes. Their value, 15 kcal mol^{-1} agrees well with the choice of 19.84 kcal mol^{-1} considering their calculated values for other molecules are also lower than the experimental values by 1-3 kcal mol^{-1}. Heublein et al. [30] calculated values of 13.57 and 49.96 kcal mol^{-1} using the '6-exp' and '6-12' potential functions of Buckingham and Lennard-Jones. For most of the molecules '6-exp' fitted better and hence 13.57 should be compared with our value. Again 19.84 kcal mol^{-1} appears to be a better value. Recently, Kolaczkowski et al. [31] showed that the boiling points have a linear relationship with the effective atomic number of halogens in a homologous series of halogen-containing compounds. Using their values of the effective atomic number for F, Cl, Br, and I as 9, 17, 21.2, and 26.7, respectively and the potential barrier heights of 4.30 and 14.7 kcal mol^{-1} for C_2F_6 [32] and C_2Cl_6 [3], we obtained a value of 19.8 kcal mol^{-1} for C_2Br_6 and 26.6 kcal mol^{-1} for C_2I_6. Mardashev et al. [29] and Heublein et al. [30] estimated 18 and 21.54 kcal mol^{-1} respectively for C_2I_6. From this analysis we have adopted 51 cm^{-1} as the torsional frequency rather than 65 cm^{-1}. For the same reason we have adopted the fundamental frequencies recommended by Shimanouchi which are presented in table 3.

No experimental $\Delta H_f^\circ(298)$ is available for C_2Br_6 and hence the estimated value as discussed in section 1.2 was adopted.

The ideal gas thermodynamic properties were calculated using the data in tables 1, 2, 3 and are presented in table 7.

6. Iodoethane (CH_3CH_2I)

The molecular parameters available are those reported by Kasuya and Oka [33] from their microwave measurements of a commercial sample of ethyl iodide (iodoethane). They had assumed $r_{CC}=1.54$ Å, $r_{CH}=1.11$ Å, and <HCH=110°. Due to the lack of more accurate data we have adopted Kasuya and Oka's values of rotational constants to obtain the moments of inertia, and of molecular parameters to calculate the reduced moment of inertia (table 2).

TABLE 7. Ideal gas thermodynamic properties of C_2Br_6

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	$\log K_f$
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.00	0.00	0.00	0.00	42.4	42.4	Infinite
100	23.72	77.86	62.55	1.53	41.9	38.0	—82.99
150	27.89	88.34	69.47	2.83	41.4	36.1	—52.64
200	30.72	96.77	75.27	4.30	41.0	34.4	37.62
273.15	33.87	106.83	82.43	6.67	32.4	32.4	—25.92
298.15	34.74	109.84	84.60	7.52	31.8	32.4	—23.76
300	34.80	110.05	84.76	7.59	31.8	32.4	—23.62
400	37.37	120.44	92.43	11.21	10.5	37.1	20.27
500	38.97	128.97	98.91	15.03	10.7	43.8	—19.13
600	40.00	136.17	104.53	18.98	11.2	50.3	—18.33
700	40.69	142.39	109.51	23.02	11.7	56.8	—17.74
800	41.18	147.86	113.97	27.12	12.2	63.2	—17.27
900	41.53	152.73	118.01	31.25	12.7	69.6	—16.89
1000	41.80	157.12	121.70	35.42	13.2	75.9	—16.58
1100	42.01	161.12	125.11	39.61	13.6	82.1	—16.31
1200	42.18	164.78	128.26	43.82	14.0	88.3	16.09
1300	42.32	168.16	131.21	48.05	14.4	94.5	—15.88
1400	42.44	171.30	133.96	52.28	14.8	100.7	—15.71
1500	42.53	174.24	136.55	56.53	15.2	106.8	—15.55

Crowder [34] reported the complete vibrational frequencies from his infrared measurements for the liquid state of CH_3CH_2I and its deuterated species. He carried out a normal coordinate analysis for confirming the frequencies. Recently Durig et al. [35] reported complete vibrational frequencies from their infrared spectral measurements in the vapor and solid state and Raman in vapor and liquid states of CH_3CH_2I and its deuterated species. They confirmed their assignments by carrying out a normal coordinate analysis. Their values agreed well with those reported by Winther and Hummel [9] from their infrared measurements (above 1300 cm^{-1}) for the vapor state of CH_3CH_2I and with those of Crowder except for ν_{16} and ν_{18} (torsion). We have adopted values of Durig et al. for the vapor state and these are presented in table 3.

Kasuya and Oka [36] from their microwave measurements reported the potential barrier to internal rotation, V_3, in CH_3CH_2I to be 3.22 kcal mol^{-1}. This gives the torsional frequency, ν_τ=228 cm^{-1}. Durig et al. [13b] observed ν_τ=258 cm^{-1} in the solid state and obtained V_3=4.43 kcal mol^{-1}. Recently Durig et al. [13a] obtained V_3=3.66 kcal mol^{-1} (from measurements of methyl torsional overtones in the Raman spectrum for the gaseous state). Between 3.22 and 3.66 kcal mol^{-1}, the former seems to be low when compared with V_3 for CH_3CH_2F (3.31), CH_3CH_2Cl (3.69), and CH_3CH_2Br (3.72). Hence we adopted V_3=3.66 kcal mol^{-1}.

Cox and Pilcher [14] have critically evaluated the enthalpies of reaction [17, 37] for CH_3CH_2I and recommended $\Delta H_f^\circ(CH_3CH_2I$, g, 298)= -2.0±0.4 kcal mol^{-1}. This value is adopted here.

The ideal gas thermodynamic properties were calculated using data from tables 1, 2, and 3 and are presented in table 8.

7. Comparison and Reliability

No experimental gaseous heat capacities and third-law entropies are available for any of these compounds. The ideal gas thermodynamic properties for CH_3CH_2Br [38, 39, 40], CH_3CBr_3 [21], C_2Br_6 [41], and CH_3CH_2I [39, 40, 42] have been reported earlier. For C_2Br_6 the earlier values reported were without the internal rotational contribution. For all these compounds, as we have used the most recent and reliable data in our calculations and the contributions to the internal rotation were obtained using the internal rotation energy levels, we feel our calculated values of the ideal gas thermodynamic properties should be more reliable. The uncertainties in the calculated values due to the uncertainties in the vibrational and torsional frequencies (assumed to be ±5 cm^{-1}) have been calculated and reported in table 9.

While using these tables one should keep in mind that for heavy molecules, the contribution due to anharmonicity effects are probably as much as 10% of the contribution of rotation and vibration and are much more significant beyond 1000 K. However, due to the lack of data needed to obtain these contributions the anharmonicity effect has be
neglected in the present work.

TABLE 8. Ideal gas thermodynamic properties of CH_3CH_2I

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔH_f°	ΔG_f°	log K_f
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.00	0.00	0.00	0.00	1.8	1.8	Infinite
100	9.52	57.58	49.22	0.84	0.4	1.5	−3.25
150	11.01	61.73	52.73	1.35	−0.2	2.2	−3.15
200	12.44	65.09	55.41	1.94	−0.8	3.0	−3.30
273.15	14.76	69.30	58.58	2.93	−1.7	4.6	−3.66
298.15	15.61	70.63	59.53	3.31	−2.0	5.2	−3.78
300	15.68	70.73	59.60	3.34	−2.0	5.2	−3.79
400	19.08	75.71	63.02	5.08	−5.1	7.9	−4.29
500	22.09	80.30	66.02	7.14	−11.2	11.7	−5.11
600	24.63	84.56	68.76	9.48	−11.8	16.1	−5.86
700	26.76	88.52	71.30	12.05	−12.3	21.1	−6.58
800	28.60	92.22	73.69	14.82	−12.6	25.8	−7.06
900	30.18	95.68	75.94	17.76	−12.9	30.7	−7.45
1000	31.56	98.93	78.08	20.85	−13.1	35.5	−7.77
1100	32.76	102.00	80.11	24.07	−13.2	40.4	−8.02
1200	33.81	104.89	82.06	27.40	−13.2	45.2	−8.24
1300	34.72	107.63	83.92	30.83	−13.2	50.1	−8.43
1400	35.51	110.24	85.71	34.34	−13.1	55.0	−8.59
1500	36.21	112.71	87.43	37.92	−13.1	59.9	−8.72

TABLE 9. Uncertainties in the ideal gas thermodynamic properties of CH_3CH_2Br, CH_3CHBr_2, CH_3CBr_3, CBr_3CBr_3 and CH_3CH_2I

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$
K	cal K^{-1} mol^{-1}			kcal mol^{-1}
		CH_3CH_2Br		
200	0.06	0.06	0.03	0.01
298.15	0.07	0.09	0.04	0.01
400	0.07	0.11	0.06	0.02
700	0.06	0.14	0.09	0.04
1000	0.04	0.16	0.11	0.06
1500	0.03	0.18	0.13	0.07
		CH_3CHBr_2		
200	0.09	0.14	0.06	0.01
298.15	0.08	0.17	0.09	0.02
400	0.08	0.19	0.12	0.03
700	0.06	0.23	0.16	0.05
1000	0.04	0.25	0.18	0.07
1500	0.02	0.26	0.21	0.08
		CH_3CBr_3		
200	0.13	0.25	0.13	0.02
298.15	0.10	0.29	0.17	0.03
400	0.08	0.32	0.21	0.04
700	0.05	0.35	0.26	0.06
1000	0.03	0.37	0.29	0.08
1500	0.02	0.38	0.32	0.09
		C_2Br_6		
200	0.18	0.90	0.61	0.06
298.15	0.12	0.96	0.72	0.07
400	0.09	0.99	0.78	0.08
700	0.04	1.02	0.88	0.10
1000	0.02	1.03	0.92	0.11
1500	0.01	1.04	0.96	0.11
		CH_3CH_2I		
200	0.06	0.07	0.03	0.01
298.15	0.07	0.10	0.05	0.01
400	0.07	0.12	0.06	0.02
700	0.06	0.15	0.09	0.04
1000	0.04	0.17	0.11	0.06
1500	0.03	0.19	0.14	0.07

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