341. *The Thermodynamic Properties of the Normal* C_2—C_5 *Alkyl Chlorides and Bromides.*

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The following thermodynamic properties of the normal C_2—C_5 alkyl chlorides and bromides have been calculated and are tabulated for the temperatures 273·16°, 298·16°, 300—1000° K: free energy function $(G^\circ - H^\circ_0)/T$, heat content function $(H^\circ - H^\circ_0)/T$, heat content $(H^\circ - H^\circ_0)$, entropy S°, and heat capacity C°_p. The values, which relate to the ideal gas state at one atmosphere pressure, were calculated for the C_2 and C_3 members by the methods of statistical thermodynamics, and, for the higher members, by an incremental method. Combination with appropriate thermochemical information yielded values for the heat, ΔH°_f, and free energy, ΔG°_f, of formation over the same temperature range.

THE thermodynamic properties of very few organic halogen compounds have been the subject of direct measurement. However, the spectroscopic thermodynamic functions for several such compounds have been calculated from complete vibrational assignments together with information about molecular structure. In the present work such calculations have been carried through for the normal C_2—C_5 alkyl chlorides and bromides, values for the ethyl and n-propyl compounds being obtained by the methods of statistical thermodynamics and, for the higher members, by a method of increments. Modern, reliable values for the heats of formation of the bromides and for ethyl chloride are available, but data on the higher chlorides are apparently several kilocalories in error.

CALCULATED THERMODYNAMIC FUNCTIONS

Throughout this work the following atomic weights [1] were used: C = 12·010; H = 1·008; Cl = 35·457; Br = 79·916. Values of fundamental constants were those of the API Research Project 44 on hydrocarbons.[2] Tabulated quantities were used in evaluating the vibrational [3]

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[1] Rossini, Wagman, Evans, Levine, and Jaffe, " Selected Values and Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, 1952.

[2] Rossini, Pitzer, Arnett, Braun, and Pimental, " Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[3] Johnston, Savedoff, and Belzer, " Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D.C., 1949.

and restricted internal rotational contributions[4] to the thermodynamic functions. The resulting total quantities for all the compounds are given in Table 1 for the free-energy function $(G^\circ - H^\circ_0)/T$, heat-content function $(H^\circ - H^\circ_0)/T$, heat content $(H - H^\circ_0)$, entropy S°, and heat capacity C°_p; all relate to one mole of the compound in the ideal gas state at one atmosphere pressure.

Ethyl Chloride.—For the vibrational contributions, the revision by Daasch, Liang, and Nielsen[5a] of earlier assignments[5b,6,7] was used; the numerical values of the frequencies (cm.$^{-1}$) were: (a') 2983, 2940, 2890, 1452 (2), 1383, 1287, 1080, 972, 676, 336; (a'') 3012, 2878, 1452, 1245, 972, 785. Molecular dimensions are available from microwave measurements:[8] C–C = 1·5495 Å; C–H = 1·110 Å; C–Cl = 1·7785 Å; ∠HCH = 110°; ∠CCCl = 110° 30′. From these, the product of the three principal moments of inertia is calculated to be $7{\cdot}010 \times 10^{-115}$ g.^{3} cm.^{6}, and the reduced moment of inertia of the methyl group is $4{\cdot}717 \times 10^{-40}$ g. cm.^{2}. The most accurate value for the barrier to free rotation of the methyl group, likewise available from microwave spectroscopy,[9] is 3560 ± 12 cal./mole.

The resulting values of the thermodynamic functions are in satisfactory agreement with those calculated previously[5a,10,11] but are considered to be more accurate by virtue of the improved data used. Additional values were calculated for comparison with measured quantities. At 200° and 280° K the heat capacity has been measured[12] as 11·82 and 14·02 cal./deg. mole, respectively; the corresponding values calculated here are 11·79 and 14·37 cal./deg. mole. Similarly, the entropy at 285·37° K derived from measurements[6] is 65·31 cal./deg. mole, whilst the value calculated here is 65·35 cal./deg. mole.

Ethyl Bromide.—A vibrational assignment for ethyl bromide was given by Sheppard[7] and, apart from one change, was adopted here. The CH_2 twisting mode was placed at 1027 cm.$^{-1}$, a value which now seems too low in view of its position in other molecules. Re-examination of the infrared spectra of the liquid and of solutions in a range of solvents revealed that the band at 1248 cm.$^{-1}$ has a shoulder on the high-frequency side, and the CH_2 twisting and wagging modes are therefore assigned at 1255 and 1245 cm.$^{-1}$. We observed only an extremely weak band at 1021 cm.$^{-1}$ (~0·06 mm. path length) which is probably due to an impurity. The numerical values of the frequencies (cm.$^{-1}$) used were: 2950 (5), 1440 (3), 1385, 1255, 1245, 1069, 960 (2), 770, 560, 292. The molecular dimensions are known[13] to be the same as for ethyl chloride, apart from C–Br = 1·9400 Å, and the product of the three principal moments of inertia is found to be $14{\cdot}92 \times 10^{-115}$ g.^{3} cm.^{6}, whilst the reduced moment of inertia of the methyl group is $4{\cdot}917 \times 10^{-40}$ g. cm.^{2}. The barrier to free rotation of the methyl group[9] is 3567 ± 30 cal./mole.

n-Propyl Chloride.—It is known[14] that the n-propyl halides exhibit rotational isomerism, the *trans*- and the (two spectroscopically indistinguishable) *gauche*-forms all being present in the liquid state at room temperature. However, for the present purpose the moments of inertia and vibrational assignment for only one of the isomers are required, since to a good approximation the thermodynamic functions for both isomers should be equal.[15] In fact, by utilising the measurements of Brown and Sheppard,[16] of Komaki *et al.*,[17] and the previous assignments for these and propane-1-thiol,[18] complete assignments for both isomers may be

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[4] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

[5] (*a*) Daasch, Liang, and Nielsen, *J. Chem. Phys.*, 1954, **22**, 1293; (*b*) Linnett, *Trans. Faraday Soc.*, 1940, **36**, 527.

[6] Gordon and Giauque, *J. Amer. Chem. Soc.*, 1948, **70**, 1506, 4277.

[7] Sheppard, *J. Chem. Phys.*, 1949, **17**, 79.

[8] Wagner and Dailey, *J. Chem. Phys.*, 1957, **26**, 1588.

[9] Lide, *J. Chem. Phys.*, 1959, **30**, 37.

[10] Howlett, *J.*, 1955, 1784.

[11] Lacher, Emery, Bohmfalk, and Park, *J. Phys. Chem.*, 1956, **60**, 492.

[12] Eucken and Franck, *Z. Elektrochem.*, 1948, **52**, 195.

[13] Wagner, Dailey, and Solimene, *J. Chem. Phys.*, 1957, **26**, 1593.

[14] Sheppard, " Advances in Spectroscopy," ed. Thompson, Interscience Publ. Inc., New York, 1959, Vol. I, p. 288.

[15] Pitzer, *J. Chem. Phys.*, 1946, **14**, 239.

[16] Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 535, 1164.

[17] Komaki, Khishima, Kuratani, Miyazawa, Shimanouchi, and Mizushima, *Bull. Chem. Soc. Japan*, 1955, **28**, 330.

[18] Pennington, Scott, Finke, McCullough, Messerly, Hossenlopp, and Waddington, *J. Amer. Chem. Soc.*, 1956, **78**, 3266.

TABLE 1.

The molal thermodynamic properties of alkyl halides in the ideal gas state at one atmosphere pressure.

T (°K)	$-(G^\circ - H^\circ_0)/T$ (cal./deg.)	$(H^\circ - H^\circ_0)/T$ (cal./deg.)	$(H^\circ - H^\circ_0)$ (kcal.)	S° (cal./deg.)	C°_p (cal./deg.)	$-\Delta H^\circ_f$ [a] (kcal.)	ΔG°_f [a] (kcal.)
Ethyl chloride							
273·16	54·42	10·32	2·82	64·74	14·14	26·41	−15·35
298·16	55·33	10·66	3·18	65·99	15·01	26·68	−14·34
300	55·39	10·69	3·21	66·08	15·07	26·70	−14·26
400	58·67	12·23	4·89	70·90	18·56	27·66	−9·96
500	61·54	13·81	6·91	75·35	21·67	28·45	−5·43
600	64·23	15·35	9·21	79·58	24·09	29·09	−0·78
700	66·70	17·19	12·03	83·89	25·50	29·31	+3·99
800	69·04	18·12	14·50	87·16	27·39	29·97	+8·80
900	71·44	19·35	17·42	90·79	30·03	30·25	+13·49
1000	73·34	20·49	20·49	93·83	31·45	30·43	+18·56
n-Propyl chloride							
273·16	61·34	13·08	3·57	74·41	19·04	31·2	−14·1
298·16	62·58	13·69	4·08	76·27	20·24	31·6	−12·6
300	62·67	13·73	4·12	76·40	20·34	31·6	−12·4
400	66·92	16·01	6·40	82·93	25·36	32·9	−5·9
500	70·75	18·34	9·17	89·09	29·73	33·9	+1·0
600	74·29	20·55	12·33	94·85	33·43	34·8	+8·0
700	77·63	22·62	15·83	100·24	36·57	35·5	+15·2
800	80·77	24·53	19·62	105·30	39·24	36·0	+22·6
900	83·77	26·29	23·66	110·06	41·57	36·3	+29·9
1000	86·62	27·93	27·93	114·55	43·59	36·5	+37·3
n-Butyl chloride							
273·16	67·04	16·23	4·43	83·26	24·15	36·1	−12·7
298·16	68·56	17·02	5·07	85·58	25·71	36·5	−10·6
300	68·67	17·07	5·12	85·74	28·84	36·6	−10·5
400	73·98	20·07	8·02	94·05	32·30	38·2	−1·5
500	78·80	23·11	11·56	101·91	37·98	39·5	+8·3
600	83·26	25·99	15·59	109·26	42·77	40·6	+17·4
700	87·49	28·68	20·07	116·16	46·85	41·4	+27·1
800	91·48	31·17	24·93	122·65	50·31	42·0	+37·0
900	95·28	33·47	30·12	128·75	53·32	42·4	+46·9
1000	98·92	35·59	35·59	134·51	55·92	42·6	+56·8
n-Pentyl chloride							
273·16	72·74	19·38	5·29	92·11	29·26	41·0	−11·3
298·16	74·54	20·35	6·06	94·89	31·18	41·4	−8·7
300	74·67	20·41	6·12	95·08	31·34	41·5	−8·4
400	81·04	24·13	9·64	105·17	39·24	43·5	+2·9
500	86·85	27·88	13·95	114·73	46·23	45·0	+15·2
600	92·23	31·43	18·85	123·67	52·11	46·3	+26·8
700	97·35	34·74	24·31	132·08	57·13	47·2	+39·0
800	102·19	37·81	30·24	140·00	61·38	47·9	+51·5
900	106·79	40·65	36·58	147·44	65·07	48·4	+63·9
1000	111·22	43·25	43·25	154·47	68·25	48·6	+76·4
Ethyl bromide							
273·16	56·65	10·57	2·89	67·22	14·57	18·76	−7·64
298·16	57·57	10·93	3·26	68·50	15·42	19·03	−6·63
300	57·66	10·97	3·29	68·63	15·50	19·04	−6·56
400	61·50	12·54	5·01	74·04	18·93	19·54	−2·44
500	64·00	14·13	7·06	78·13	21·98	20·76	+2·27
600	66·70	15·66	9·39	82·36	24·54	21·38	+6·94
700	69·23	17·08	11·96	86·31	26·69	21·86	+11·28
800	71·60	18·40	14·72	90·00	28·55	22·23	+16·52
900	73·86	19·62	17·66	93·48	30·16	22·49	+21·36
1000	75·96	20·74	20·74	96·70	31·56	22·67	+26·27
n-Propyl bromide							
273·16	63·66	13·52	3·69	77·18	19·45	25·33	−8·22
298·16	64·94	14·14	4·22	79·08	20·66	25·65	−6·69
300	65·02	14·17	4·25	79·19	20·73	25·67	−6·57

TABLE 1. (*Continued*).

T (°K)	$-(G° - H°_0)/T$ (cal./deg.)	$(H° - H°_0)/T$ (cal./deg.)	$(H° - H°_0)$ (kcal.)	$S°$ (cal./deg.)	$C°_p$ (cal./deg.)	$-\Delta H°_f$ [a] (kcal.)	$\Delta G°_f$ [a] (kcal.)
			n-Propyl bromide				
400	69·40	16·45	6·58	85·85	25·70	26·95	0·00
500	73·32	18·74	9·37	92·06	30·02	28·00	+6·86
600	76·94	20·93	12·56	97·87	33·66	28·84	+13·90
700	80·30	22·98	16·09	103·28	36·76	29·48	+21·11
800	83·52	24·87	19·89	108·38	39·41	29·98	+28·34
900	86·66	26·67	24·01	113·33	41·74	30·26	+35·55
1000	89·89	28·22	28·22	118·11	43·70	30·53	+42·55
			n-Butyl bromide				
273·16	69·36	16·67	4·55	86·03	24·56	28·91	−5·53
298·16	70·92	17·47	5·21	88·39	26·13	29·32	−3·45
300	71·02	17·51	5·25	88·53	26·23	29·35	−3·27
400	76·46	20·51	8·20	96·97	32·64	30·95	+5·68
500	81·37	23·51	11·76	104·88	38·27	32·26	+14·99
600	85·91	26·37	15·82	112·28	43·00	33·29	+24·54
700	90·16	29·04	20·33	119·20	47·04	34·09	+34·26
800	94·23	31·51	25·21	125·74	50·48	34·67	+44·04
900	98·17	33·85	30·47	132·02	53·49	35·01	+53·82
1000	102·19	35·88	35·88	138·07	56·03	35·30	+63·37
			n-Pentyl bromide				
273·16	75·06	19·82	5·41	94·88	29·67	33·88	−4·22
298·16	76·90	20·80	6·20	97·70	31·60	34·37	−1·87
300	77·02	20·85	6·26	97·87	31·73	34·41	−1·34
400	83·52	24·57	9·83	108·12	39·58	36·33	+9·98
500	89·42	28·28	14·14	117·70	46·52	37·89	+21·74
600	94·88	31·81	19·09	126·69	52·34	39·12	+33·80
700	100·02	35·10	24·57	135·12	57·32	40·07	+46·04
800	104·94	38·15	30·52	143·09	61·55	40·75	58·36
900	109·68	41·03	36·93	150·71	65·24	41·14	70·71
1000	114·49	43·54	43·54	158·03	68·36	41·45	82·80

[a] Standard heat and free energy of formation by the reaction (X = Cl or Br): $n\mathrm{C(gr)} + (n + \tfrac{1}{2})\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{X_2(g)} = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{X(g)}$.

made; the resulting frequencies are given in Table 2. An approximate sum rule [19] for rotational isomers requires that $\sum\nu^2$ (*trans*) = $\sum\nu^2$ (*gauche*); for the seven frequencies which are split sufficiently to be resolved in the observed spectra the terms are $4{\cdot}99 \times 10^6$ and $5{\cdot}14 \times 10^6$ for the *trans*- and the *gauche*-isomers, respectively.

The formalised procedure of Kilpatrick and Pitzer [20] was used to evaluate the moments of inertia, with conventional values of bond angles and lengths for the *trans*-configuration: C–H = 1·09 Å; C–C = 1·54 Å; C–Cl = 1·78 Å; all angles tetrahedral. The product of the principal moments of inertia was found to be $4{\cdot}334 \times 10^{-114}$ g.^{3} cm.^{6}, and the reduced moments of inertia of the methyl and the ethyl group were found to be $4{\cdot}574 \times 10^{-40}$ and $22{\cdot}89 \times 10^{-40}$ g. cm.^{2}, respectively.

The restricted internal rotation of the methyl group was then treated as a simple three-fold barrier and the height taken as 3100 cal./mole after consideration of the values for similar compounds. For the internal rotation about the central C–C bond a potential function of the following form was assumed:

$$V(\phi) = V_0/2\ (1 - \cos 3\phi),\ 0 < \phi < \pi/3;\ 5\pi/3 < \phi < 2\pi,$$
$$V(\phi) = V_0/2\ (1 - \cos 3\phi) + \Delta E,\ \pi/3 < \phi < 5\pi/3,$$

V_0 being the barrier height, ϕ the angle of rotation measured from the *trans*-configuration, and ΔE the energy difference between the *trans*- and the *gauche*-forms. The contributions to the thermodynamic functions were then calculated as those arising from a simple three-fold barrier of height V_0, together with those calculated by considering the equilibrium between the rotational isomers.[21] This equilibrium is determined by ΔE, the energy change of the reaction

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[19] Mizushima, Shimanouchi, Nakagawa, and Miyake, *J. Chem. Phys.*, 1953, **21**, 215.

[20] Kilpatrick and Pitzer, *J. Chem. Phys.*, 1949, **17**, 1064.

[21] Pitzer, *J. Chem. Phys.*, 1937, **5**, 473.

trans ⟶ *gauche*, and by the entropy change, assumed to be $\boldsymbol{R}$ ln 2 since there are two *gauche*-conformations and only one *trans*-conformation. Values of ΔE are available from spectroscopic measurements: $-0{\cdot}05 \pm 0{\cdot}15$ (ref. 17) and $-0{\cdot}05 \pm 0{\cdot}07$ kcal./mole (ref. 22); the value $-0{\cdot}05$ kcal./mole was used. The value of V_0 was taken as 2900 cal./mole by analogy with that for similar compounds. It follows from this treatment that the vibrational contribution to the heat capacity of the isomers should be equal: at 500° K the contributions are 17·68 and 17·58 cal./deg. mole for the *trans*- and the *gauche*-forms, respectively.

TABLE 2.

Vibrational assignments (frequencies in cm.$^{-1}$) for n-propyl chloride and bromide.

	n-Propyl chloride		n-Propyl bromide			n-Propyl chloride		n-Propyl bromide	
Mode	*trans*	*gauche*	*trans*	*gauche*	Mode	*trans*	*gauche*	*trans*	*gauche*
Skeletal bend ...	249	292	223	272	CH_2 twist	1162	1208	1146	1200
	368	426	313	402	CH_2 wag	1259	1259	1228	1228
ν(CX)	729	650	694	564	CH_2 twist	1300	1300	1286	1286
CH_2 rock	749	790	740	778	CH_2 wag	1340	1340	1327	1340
CH_2 rock	858	858	840	840	CH_3 deform. ...	1378	1378	1380	1380
CH_3 rock	898	898	890	890	2 CH_2 bend ...	1440	1440	1440	1440
ν(CC)	1038	1038	1030	1032	2 CH_3 deform.	1460	1460	1456	1456
ν(CC)	1063	1088	1040	1085					
CH_3 rock	1105	1088	1109	1085	7 ν(CH) (average) ...	2950	2950	2950	2950

n-Propyl Bromide.—These calculations were carried out as for n-propyl chloride. The vibrational assignments for the *trans*- and the *gauche*-forms are given in Table 2 and yield $\sum \nu^2$ (*trans*) $= 4{\cdot}80 \times 10^6$ and $\sum \nu^2$ (*gauche*) $= 4{\cdot}95 \times 10^6$ for the seven different frequencies. The vibrational contributions to the heat capacity at 500° K were found to be 17·96 and 17·86 cal./deg. mole for the *trans*- and the *gauche*-forms, respectively. The same conventional values of bond angles and lengths were used, with C–Br = 1·94 Å; for the *trans*-configuration the product of the principal moments of inertia was $9{\cdot}057 \times 10^{-114}$ g.^{3} cm.^{6}, whilst the reduced moments of the methyl and ethyl groups were 4·577 and $29{\cdot}17 \times 10^{-40}$ g. cm.^{2}, respectively. The barrier heights for the internal rotations were assumed identical with those in n-propyl chloride.

Three spectroscopic determinations of the energy difference between the rotational isomers yielded the values $-0{\cdot}1 \pm 0{\cdot}2$ (ref. 17), $-0{\cdot}28 \pm 0{\cdot}1$ (ref. 22), and *ca.* 0 kcal./mole (ref. 23). From these results the value $-0{\cdot}2$ kcal./mole was chosen. Changing this value by 0·1 kcal./mole affects the contribution to the entropy by 0·02 cal./deg. mole at 300° K and by 0·01 cal./deg mole at 1000° K; the effect on the other functions is negligible.

n-Butyl and n-Pentyl Chlorides and Bromides.—The values of a thermodynamic property P [$(G° - H°_0)/T$, $C°_p$, etc.] for members of an homologous series $H{\cdot}[CH_2]_n{\cdot}X$ may be written

$$P\,(H{\cdot}[CH_2]_n{\cdot}X) = A + Bn + \delta$$

where A is a constant for a particular end group X, B is the methylene increment, constant for all normal alkyl series, and δ is a term which is small for the lower members but becomes zero for higher members. For the higher halides considered here, $n > 3$, and to the present degree of approximation δ may be ignored. Values for n-butyl and n-pentyl chloride and bromide were therefore obtained by adding the appropriate number of methylene increments to the values for the n-propyl halide. The increments given by Person and Pimental[24] were used with additional calculated values for 273·16° K: $(G° - H°_0)/T$, $-5{\cdot}697$; $(H° - H°_0)/T$; 3·152; $C°_p$, 5·111 cal./deg. mole. The possible errors arising from this procedure have been estimated previously.[25]

HEAT AND FREE ENERGY OF FORMATION

Three recent investigations over a range of temperatures have yielded values for the heat of formation of ethyl chloride at 298·16° K: $-25{\cdot}74$,[11] $-26{\cdot}7$,[26] and $-26{\cdot}66$ kcal./mole.[10]

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[22] Pentin and Tatevskii, *Doklady Akad. Nauk S.S.S.R.*, 1956, **108**, 290.

[23] Yoshino and Bernstein, *Canad. J. Chem.*, 1957, **35**, 339.

[24] Person and Pimental, *J. Amer. Chem. Soc.*, 1953, **75**, 532.

[25] Green, *J. Appl. Chem.*, 1961, **11**, 397.

[26] Lane, Linnett, and Oswin, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361.

No significant change is caused by use of the thermodynamic properties calculated above to reduce the data, and, by giving greatest weight to the last two values derived from equilibrium measurements, the value −26·68 ± 0·30 kcal./mole is here selected as the " best " value. Smith *et al.*[27] have revised and corrected the measured heats of combustion of n-propyl, n-butyl, and n-pentyl chloride, and from these the heats of formation listed in the second column of Table 3 have been derived; standard values [1] for the heats of formation of carbon dioxide and water and the interpolated value [1] of −39·884 kcal./mole for the heat of formation of HCl, $600H_2O$, were used. Examination of the results in the light of regularities established for the paraffins,[2] normal alcohols,[25] other organic oxygen compounds,[28] and for the corresponding bromides (see below) reveals that the values for the alkyl chlorides are in error by probably several kilocalories. Values have, therefore, been estimated with the aid of these regularities and other work,[29] and are given in Table 3. The heats of vaporisation at 298·16° K also listed were derived from vapour-pressure data, greatest weight being given to the values obtained from the constants of the Antoine equations fitted to the smoothed vapour pressures.[30] Values for the heats of formation of the gaseous alkyl chlorides at 298·16° K were then combined with the calculated thermodynamic functions, and the similar quantities for carbon [2] (graphite), hydrogen [2] (gas), and chlorine [31] (gas), to obtain the heat and free energy of formation over the whole temperature range; values of ΔH°_0, the change in heat content for the formation reaction at 0° K, are given in Table 3.

TABLE 3.

Heats of formation and vaporisation (kcal./mole) of alkyl halides at 298·16° K.

	$-\Delta H_f$ [1]		ΔH_{vap}	$-\Delta H^\circ_f(g)$			
	Lit.	This work	This work	Lit.	This work		$-\Delta H^\circ_0(g)$
C_2H_5Cl	—	—	6·02	See text	26·68		23·20
C_3H_7Cl	42·72	38·6	7·01	—	31·6		26·7
C_4H_9Cl	43·90	44·6	8·05	—	36·5		30·4
$C_5H_{11}Cl$	52·00	50·7	9·15	—	41·5		34·1
					(*a*)	(*b*)	(*b*)
C_2H_5Br	—	22·10	6·74	15·3	15·36	19·03	15·56
C_3H_7Br	29·73 ± 0·34	29·73	7·75	21·98	21·98	25·65	20·86
C_4H_9Br	34·47 ± 0·31	34·47	8·82	25·65	25·65	29·32	23·25
$C_5H_{11}Br$	40·72 ± 0·35	40·55	9·85	30·87	30·70	34·37	27·02
$C_6H_{13}Br$	46·48 ± 0·39	46·53	10·90	35·58	35·63	39·30	30·67
$C_7H_{15}Br$	52·24 ± 0·39	52·48	11·93	40·31	40·55	44·22	34·30
$C_8H_{17}Br$	58·61 ± 0·55	58·44	12·96	45·65	45·48	48·15	36·95

(*a*) Heat of formation by the reaction $n\text{C(gr)} + (n + \tfrac{1}{2})\text{H}_2\text{(g)} + \tfrac{1}{2}\text{Br}_2\text{(l)} = \text{C}_n\text{H}_{2n+1}\text{Br(g)}$. (*b*) Heat of formation by the reaction $n\text{C(gr)} + (n + \tfrac{1}{2})\text{H}_2\text{(g)} + \tfrac{1}{2}\text{Br}_2\text{(g)} = \text{C}_n\text{H}_{2n+1}\text{Br(g)}$.

For ethyl bromide the most reliable value for the heat of formation is that derived from measurements [26] of the equilibrium with ethylene and hydrogen bromide. With the results of the present work and known values for ethylene [2] and hydrogen bromide,[32] the entropy change, for the reaction with the halide as product, is found to be −31·89 cal./deg. mole at 500° K, and −31·85 cal./deg. mole at 600° K. The measured equilibrium constants then give the following values for the heat content change of the reaction: at 515·3° K, −19·50; 533·2°, −19·41; 547·9°, −19·36; 560·4°, −18·96; 573·0°, −19·39 kcal./mole; from which the mean value at 550° K is taken to be −19·41 ± 0·3 kcal./mole; corrected to 298·16° K this becomes −19·20 kcal./mole. With the accepted values [1] for the heats of formation of hydrogen bromide and ethylene, the heat of formation of gaseous ethyl bromide from carbon (graphite), hydrogen (gas), and bromine (liquid) is found to be −15·36 ± 0·30 kcal./mole.

Bjellerup [33] recently published measurements of the heats of combustion of the normal

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[27] Smith, Bjellerup, Krook, and Westermark, *Acta Chem. Scand.*, 1953, **7**, 65.

[28] Green, *Quart. Rev.*, 1961, **15**, 125.

[29] Benson and Buss, *J. Chem. Phys.*, 1958, **29**, 546.

[30] Manufacturing Chemists Association Research Project on Properties of Chemical Compounds, Pittsburgh, Pennsylvania, Tables 23–10–2, k; 23–11–2, k, 1956.

[31] Evans, Munson, and Wagman, *J. Res. Nat. Bur. Stand.*, 1955, **55**, 147.

[32] Gordon and Barnes, *J. Chem. Phys.*, 1933, **1**, 692.

[33] Bjellerup, *Acta Chem. Scand.*, 1961, **15**, 121, 231.

C_3—C_8 alkyl bromides and considered the derived heats of formation in relation to other work. Slightly different values for the heats of vaporisation at 298·16° K from those given by Bjellerup have been used here, in the light of additional smoothed vapour-pressure data;[30] the values chosen (kcal./mole) satisfy the expression $\Delta H_{\mathrm{vap}}(C_nH_{2n+1}Br) = 4{\cdot}64 + 1{\cdot}04n$ ($n > 2$). The resulting smoothed values for the heats of formation of the gaseous alkyl bromides from carbon (graphite), hydrogen (gas), and bromine (liquid) are given in the sixth column of Table 3 and may be expressed (kcal./mole) by:

$$-\Delta H_f(g),\ C_nH_{2n+1}Br = 6{\cdot}06 + 4{\cdot}926n.$$

This expression differs slightly from the equivalent form given by Bjellerup[33] but the corresponding values for the heats of formation of the liquid halides are seen from Table 3 to agree within experimental error with the measured quantities.

For the alkyl bromides at temperatures above 300° K a more suitable standard state for bromine is the ideal diatomic gas. Taking[1] 7·34 kcal./mole as the heat of formation of bromine gas at 298·16° K leads to the values in the seventh column of Table 3 for the heats of formation of the halides from carbon (graphite), hydrogen (gas), and bromine (gas). These were then combined with the calculated thermodynamic functions and the similar quantities for the elements[2,31] to obtain the heat and free energy of formation over the whole temperature range.

TABLE 4.

Entropies (cal./deg. mole) and free energies of formation (kcal./mole) of alkyl halides at 298·16° K.

	$\Delta G^\circ_f(g)$[a]	S (liq.)	ΔG_f(liq.)[b]
C_2H_5Br	−6·30	46·77	−6·57
C_3H_7Br	−6·37	56·48	−7·38
C_4H_9Br	−3·10	64·60	−4·83
$C_5H_{11}Br$ ...	−1·21	72·81	−3·64
$C_6H_{13}Br$ ...	+0·79	80·9	−2·3
$C_7H_{15}Br$ ...	+2·81	89·1	−1·0
$C_8H_{17}Br$ ...	+4·81	97·3	+0·3

[a] Free energy of formation by the reaction $nC(gr) + (n + \frac{1}{2})H_2(g) + \frac{1}{2}Br_2(l) = C_nH_{2n+1}Br(g)$.
[b] Free energy of formation by the reaction $nC(gr) + (n + \frac{1}{2})H_2(g) + \frac{1}{2}Br_2(l) = C_nH_{2n+1}Br(l)$.

TABLE 5.

Constants in expressions for heat and free energy (kcal./mole) of formation of alkyl halides $C_nH_{2n+1}X$.

Temp. (°K)	$-\Delta H^\circ_f(g)$			$\Delta G^\circ_f(g)$		
	A (X = Cl)	A (X = Br)	B	$-C$ (X = Cl)	$-C$ (X = Br)	D
273·16°	16·8	9·68	4·82	18·5	11·47	1·45
298·16	16·82	9·72	4·93	18·6	11·59	2·01
300	16·9	9·76	4·93	18·7	11·60	2·05
400	17·2	10·08	5·25	19·2	12·12	4·43
500	17·5	10·34	5·51	19·7	12·66	6·88
600°	17·8	10·57	5·71	20·1	13·10	9·38
700	18·0	10·82	5·85	20·5	13·51	11·91
800	18·2	11·00	5·95	20·8	13·89	14·45
900	18·4	11·14	6·00	21·1	14·34	17·01
1000	18·5	11·35	6·02	21·5	15·05	19·57

By employing the value[34] of 36·25 cal./deg. mole for the entropy of liquid bromine at 298·16° K, the free energies of formation of the bromides from liquid bromine were next calculated for that temperature. By combining the calculated entropies for gaseous halides with entropies of vaporisation ($\Delta H_{\mathrm{vap}}/298{\cdot}16$; see the values of Table 3) and vapour-pressure data,[30] the entropies of the liquid halides at 298·16° K were obtained. [For ethyl bromide a gas imperfection term of 0·08 cal./deg. mole was included, calculated from the Berthelot equation of state and values[35] for the critical temperature (503·9° K) and pressure (61·5 atm.).] The entropies of the liquid compounds were then combined with the corresponding heat quantity to obtain the free energies of formation of the liquid bromides from liquid bromine at 298·16° K. The values are given in Table 4.

[34] Stull and Sinke, " Thermodynamic Properties of the Elements," Amer. Chem. Soc., Washington, 1956.

[35] Kobe and Lynn, *Chem. Rev.*, 1953, **52**, 121.

Finally, the constants in the expressions

$$-\Delta H^\circ_f(g) = A + Bn;\ n > 3$$
$$\Delta G^\circ_f(g) = C + Dn;\ n > 3$$

for the heat and free energy of formation (kcal./mole) of gaseous $C_nH_{2n+1}Br$ from gaseous bromine were evaluated for the whole temperature range and are given in Table 5.

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