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A New Generalized Bond Energy/Group Contribution Scheme for Calculating the Standard Heat of Formation of Monomers and Polymers. Part IV. Halocarbons*

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ABSTRACT

A self-consistent set of bond energy terms permitting estimation of heats of formation of halogen compounds is evolved. The overall precision attained is ±0.7 kcal/mole, which is considerably better than that of the experimental data. Heats of formation of halogen containing monomers and polymers, and heats of polymerization are calculated.

INTRODUCTION

The generalized bond-energy scheme developed earlier in three parts for the hydrocarbons [1] has been extended to halogen compounds containing only carbon and hydrogen besides the halogen. The existing

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experimental data on halogen compounds are relatively imprecise, especially for fluorine compounds, in comparison to the hydrocarbons. The overall uncertainty in the experimental data on halocarbons is about ±1.0 kcal/mole, and the precision achieved by the scheme is around ±0.7 kcal/mole.

The data on heats of formation of fluorine compounds required a revision in terms of the new values of $\Delta H_f^\circ(g)$ for CF_4, HF(aq), and NaF(c) which are the key compounds in fluorine thermochemistry. Although this revision has been accomplished by pioneering workers [2-4], some uncertainty exists in the values of $\Delta H_f^\circ(g)$ of these key compounds [5], and hence in the absolute values of the standard heat of formation of the fluorine compounds. Besides, the absolute energy of the C—F bond (E° in Table 2) depends on the value of bond dissociation energy of the fluorine molecule. This value has been authoritatively revised in a recent publication [6] and therefore adopted by us. For bond-energy correlation in this work, the data compiled by Cox and Pilcher [2] and Lacher and Skinner [3] have been mainly employed since the values of key compounds used by these authors are in conformity with the observations made by Armstrong [5] after a special study of the key data. The selected data are mostly from Ref. 2 with some revision, wherever necessary, on the basis of new work published after 1968.

The basic C—C and C—H bond-energy terms employed in this work are listed in Table 1. These are taken from earlier work [1] with a revision of terms pertaining to sp-carbon (C^1) so as to allow better coordination and link with the nitriles containing the carbon atom of similar hybridization, and with other nitrogen compounds. The values in Table 1 will be strictly adhered to in all future parts of the scheme when extended to oxygen, sulfur, and nitrogen compounds.

DERIVATION OF BOND-ENERGY TERMS

The procedure of deriving bond-energy terms and the nomenclature for these bonds are the same as in the previous work [1]. This consists of identification of the various molecular structural factors that affect the heat of formation, followed by grouping the compounds with similar structural features, and averaging the excess energy ascribable to a particular new type of bond. The energy terms so derived are listed in Table 2, which also identifies the compounds, lettered and numbered according to Table 3, from which these terms have been derived. The last section of Table 2 contains bond energies of the key compounds, most of which have been very authentically confirmed [7].

TABLE 1. Basic Bond-Energy Terms and Specific Interactions Related to Hydrocarbons, Adapted for the General Bond-Energy Scheme

Bond	ΔH_f° (g) (kcal/mole)	Bond	ΔH_f° (g) (kcal/mole)
Carbon-Hydrogen Bonds		C^2-C^ϕ	-10.75
C^3-H'	-1.78	$C^\phi-C^\phi$	-10.75
C^3-H''	-2.68	C^1-C^3	-15.00
C^3-H'''	-3.48	C^1-C^2	-21.74
C^2-H'	-5.68	C^1-C^ϕ	-20.10
C^2-H''	-6.38	C^1-C^1	-32.90
$C^\phi\underset{\cdot\cdot}{-}H$	-6.80	$C^\phi\underset{\cdot\cdot}{-}C^\phi$	+10.10
C^1-H	-15.85	$C^\phi\underset{\cdot\cdot}{-}C^\phi_*$	+7.03
Carbon-Carbon Bonds		$C^\phi_*\underset{\cdot\cdot}{-}C^\phi_*$	+1.53
$C^3_1-C^3_1$	+0.45	$C^2=C^2$	+38.00
$C^3_1-C^3_2$	+0.45	$C^0=C^2$	+36.00
$C^3_2-C^3_2$	+0.45	$C^1\equiv C^1$	+85.00
$C^3_3-C^3_2$	+0.60	1-3 Steric Interactions	
$C^3_4-C^3_2$	+1.30	$C^3_4(C)C^3_3$	+1.74
$C^3_3-C^3_3$	+1.95	$C^3_4(C)C^3_4$	+5.26
$C^3_4-C^3_3$	+3.72	Other Interactions: Ref. 1b	
$C^3_4-C^3_4$	+6.54	Ring-Strain Corrections: Ref. 1c	
C^2-C^3	-4.40		
$C^\phi-C^3$	-4.24		
$C^2-C^3_4$	-2.50		
$C^\phi-C^3_4$	-2.50		
C^2-C^2	-12.97		

TABLE 2. Bond Energy Terms and Nonbonded Interactions for Calculating ΔH_f°(g, 298.15°K) of Halocarbons

No.	Bond/group[a]	ΔH_f°(g) (kcal/mole)	Bond strength[b] (E°), (kcal/mole)	Compounds from which derived:[c] Remarks
	Carbon-Fluorine Bonds			
1	C^3-F'	-45.96	104.2	A (6,24,25,26)
2	C^3-F''	-48.81	107.1	A (6,24,25,26)
3	C^3-F'''	-53.97	112.2	A (6,24,25,26)
4[d]	C^3-F^4	-55.83	114.0	A (1); for CF_4 only
5	$(H)C^3-F'$	-47.31	105.6	A (13,15,16)
6	$(H)C^3-F''$	-51.48	109.8	A (3,9,11,12)
7	$(H)C^3-F'''$	-54.84	113.1	A (2); for CHF_3 only
8	C^2-F'	-52.15	110.4	A (7,23)
9	C^2-F''	-48.85	107.1	A (5)
10[e]	$C^{\phi}-F^n$	$-[55.4-(1.2)n]$	$[113.7-(1.2)n]$	A (17,18,19,21,22,27,28)
	Hydrogen-Fluorine (1-2)-Interactions			
11	$(C^3_{H}\ldots C^3_{F''})$	-2.10	2.10	A (3,8,11,12)
12	$(C^2_{H''}\ldots C^2_{F''})$	-5.00	5.00	A (10); for $CH_2{:}CF_2$ only

	Carbon-Chlorine Bonds			
13	C^3_1-Cl'	-11.33	83.2	B (13,16,21,23,27,29,30)
14	C^3_2-Cl'	-12.59	84.5	B (15,24,32)
15	C^3_3-Cl'	-14.10	86.0	B (23,31)
16	C^3-Cl''	-8.82	80.7	B (3)
17	C^3-Cl'''	-7.67	79.6	B (2)
18^d	C^3-Cl^4	-5.73	77.6	B (1); for CCl_4 only
19	C^2-Cl'	-12.75	84.7	B (8,9,17)
20	C^2-Cl''	-10.18	82.1	B (5)
21^e	$C^\phi-Cl^n$	-[14.80-(0.53)n]	[86.7-(0.53)n]	B (33,34,35,36,37)
22	C^1-Cl	-21.8	93.7	Estimate from cyanogen chloride
23	$(F'')C^3-Cl$	-9.13	81.0	E (1,4,5,10,11)
24	$(F''')C^3-Cl$	-7.39	79.3	E (1)
	Hydrogen-Chlorine (1-2)-Interactions			
25	$(C^3_H \ldots C^3_{Cl''})$	-0.82	0.8	B (11,12,14,22)
26	$(C^2_{H''} \ldots C^2_{Cl'})$ $(C^2_{H'} \ldots C^2_{Cl''})$	-1.50	1.5	B (6,10,18)
27	$(C^2_{H''} \ldots C^2_{Cl''})$	-2.14	2.1	B (7); for CH_2:CCl_2 only.

continued

TABLE 2 (continued)

No.	Bond/group[a]	ΔH_f°(g) (kcal/mole)	Bond strength[b] (E°), (kcal/mole)	Compounds from which derived:[c] Remarks
	Carbon-Bromine Bonds			
28	C_1^3—Br'	-0.43	70.0	C (2,3,7,10,11,12,13,16)
29	C_2^3—Br'	-1.71	71.3	C (4,5,6,8)
30	C_3^3—Br'	-1.93	71.5	C (9)
31	C^2—Br	-0.85	70.4	C (14)
32	C^ϕ—Br	-1.40	71.0	C (15)
	(C^3—Br''), (C^3—Br'''), (C^3—Br^4): No thermochemical data available			
33	(F')C^3—Br (F'')C^3—Br	+2.71	64.9	E (12,13,14)
34	(F''')C^3—Br	+6.91	60.7	E (2)
	Carbon-Iodine Bonds			
35	C_1^3—I'	+13.14	55.1	D (4,5,7,11)
36	C_2^3—I'	+11.92	56.4	D (6,8,9,13)
37	C_3^3—I'	+12.47	55.9	D (10)
38	C^3—I''	+16.78	51.6	D (2)
39	C^3—I'''	+17.39	51.0	D (3)
40	C^ϕ—I	+12.92	55.4	D (12,14,15,16,17,18,19)

	(C^2-I)	(+12.9)		No thermochemical data available. A probable value.
41	$(F)C^3-I$	+21.40	46.9	E (3)
	Other Halogen Bonds (Key Data)			Refs.
1	$H-H$	0.00	104.2	[7]
2	$F-F$	0.00	30.9	[6]
3	$Cl-Cl$	0.00	58.0	[7]
4	$Br-Br$	0.00	53.5	[7]
5	$I-I$	0.00	51.0	[7]
6	$H-F$	-65.00	132.6	[2,5,6]
7	$H-Cl$	-22.06	103.2	[7]
8	$H-Br$	-8.70	87.5	[7]
9	$H-I$	+6.30	71.3	[7]
10	$Cl-F'$	-15.00	59.5	[6]
11	$Cl-F'''$	-13.12	38.3	[8]
12^d	$Cl-F^5$	-11.34	32.6	[9]
13	$Br-F'$	-14.00	56.2	[10]
14	$Br-F'''$	-20.37	44.7	[10]
15^d	$Br-F^5$	-20.50	41.3	[9]
16	$I-F'$	-22.65	63.3	[10]
17^d	$I-F^5$	-39.32	59.9	[9]

continued

TABLE 2 (continued)

No.	Bond/group[a]	$\Delta H_f^\circ(g)$ (kcal/mole)	Bond strength[b] (E°), (kcal/mole)	Compounds from which derived:[c]	Remarks
18[d]	$\mathrm{I{-}F^{7}}$	-32.81	51.9	[10]	
19	I—Cl	+4.18	50.4	[10]	
20	I—Br	+9.77	42.5	[10]	
21	$\mathrm{C}\underset{\cdot\cdot}{-}\mathrm{F}''$	-22.25	123.4	[29]	

[a] For nomenclature of bonds, refer to previous work [1].

[b] Bond-strength calculated without reducing $\Delta H_f^\circ(g)$ to absolute zero is a close approximation of the absolute bond energy, E_0°. Heats of atomization of elements have been taken from CODATA Organization Report [7] except for fluorine [6].

[c] Letters indicates the subheads of Table 3.

[d] Superscript primes replaced by numerals when three is exceeded.

[e] n = number of halogen substitutions in the aromatic nucleus.

TABLE 3. Heats of Formation (Ideal Gas, 298.15°K) of Halocarbons: Comparison of Observed and Calculated Data

No.	Compound	$\Delta H^\circ_f(x)$[a] exptl (kcal/mole)	$\Delta H^\circ_f(g)$[b] obs (kcal/mole)	$\Delta H^\circ_f(g)$ calc (kcal/mole	Error[c] (obs-calc) (kcal/mole)	Refs.[d]
			(A) Fluorine Compounds			
1	Carbon tetrafluoride	-223.3 ± 0.5(g)	-223.3 ± 0.5	-223.3	0.0	[2]
2	Trifluoromethane	-166.3 ± 0.7(g)	-166.3 ± 0.7	-166.3	0.0	[2]
3	Difluoromethane	-108.1 ± 0.3(g)	-108.1 ± 0.3	-108.3	+0.2	[2]
4	Fluoromethane	-55.9 ± 0.5(g)	-55.9 ± 0.3	-57.8	+1.9	[4]
5	Tetrafluoroethylene	-157.4 ± 0.5(g)	-157.4 ± 0.8	-157.4	0.0	[(2)]
6	Poly(tetrafluoroethylene)	-199.1 ± 0.5(s)	-195.0 ± 0.7	-194.3	-0.7	[(2, 12-14), 15]
7	Trifluoroethylene	-117.4 ± 2.0(g)	-117.4 ± 2.0	-117.5	+0.1	[(2)]
8	1,1,1-Trifluoroethane	-178.2 ± 0.4(g)	-178.2 ± 0.5	-178.2	0.0	[(2)]
9	1,1,2-Trifluoroethane	-162.8 ± 3.0(g)	-162.8 ± 3.0	-161.2	-1.6	[(2, 3)]
10	1,1-Difluoroethylene	-82.5 ± 1.4(g)	-82.5 ± 1.0	-82.5	0.0	[(2, 3)]
11	Poly(vinylidene fluoride)	-116.1 ± 0.5(s)	(-111.8 ± 1.0)	-110.5	-1.3	[(12), 15]
12	1,1-Difluoroethane	-118.8 ± 2.0(g)	-118.8 ± 2.0	-118.9	+0.1	[2]
13	Fluoroethane		(-62.5 ± 0.5)[e]	-62.2	-0.3	[3, 4]
14	1,1,1-Trifluoropropene	-146.9 ± 1.6(g)	-146.9 ± 1.6	-146.8	-0.1	[2]

continued

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(x)^a$ exptl (kcal/mole)	$\Delta H_f^\circ(g)^b$ obs (kcal/mole)	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Error^c (obs-calc) (kcal/mole)	Refs.^{d}
15	1-Fluoropropane	-67.6 ± 0.5(g)	-67.6 ± 0.8	-67.6	0.0	[2]
16	2-Fluoropropane	-69.0 ± 0.5(g)	-69.0 ± 0.8	-69.1	+0.1	[3, 4]
17	Hexafluorobenzene	-237.0 ± 0.3	-228.5 ± 0.5	-228.6	+0.1	[2]
18	Pentafluorobenzene	-201.3 ± 0.4	-192.7 ± 0.4	-193.2	+0.5	[2]
19	1,4-Difluorobenzene	-81.8 ± 0.5	-73.3 ± 0.5	-73.6	+0.3	[2]
20	1,3-Difluorobenzene	-82.3 ± 0.5	-74.0 ± 0.5	-73.6	-0.4	[2]
21	1,2-Difluorobenzene	-78.9 ± 0.5	-70.3 ± 0.5	-73.6	(+3.3)	[2]
22	Fluorobenzene	-36.0 ± 0.3	-27.8 ± 0.5	-27.6	-0.2	[2]
23	Decafluorocyclohexene	-469.7 ± 0.5	-462.4 ± 0.5	-462.2	-0.2	[(2)]
24	Tetradecafluoromethylcyclohexane	-701.1 ± 1.2	-693.0 ± 1.2	-692.8	-0.2	[2]
25	Hexadecafluoroheptane	-818.0 ± 1.0	-809.3 ± 0.5	-809.2	-0.1	[2]
26	Hexadecafluoroethylcyclohexane	-799.1 ± 1.3	-789.9 ± 1.3	-790.4	+0.5	[2]
27	2,3,4,5,6-Pentafluorotoluene	-211.3 ± 0.4	-201.5 ± 1.0	-201.1	-0.4	[2]
28	4-Fluorotoluene	-44.8 ± 0.5	-35.4 ± 0.5	-35.5	+0.1	[2-4]
	Standard deviation		±1.2		±0.6	

	Exceptional cases					
29	Hexafluoroethane	-321.3 ± 0.9(g)	-321.3 ± 0.9	-323.4	+2.1	[2]
30	Hexafluorocyclobutene	-235.9 ± 1.0(g)	-235.9 ± 1.0	-239.7	+3.8	[3]
31	Hexafluorobutadiene	-224.2 ± 2.0(g)	-224.2 ± 2.0	-236.7	+12.5	[3]
32	Trifluoromethylbenzene	-152.2 ± 0.2	-143.2 ± 0.2	-139.6	-3.6	[2]
33	Trifluoromethyl-3-fluorobenzene	-198.5 ± 0.2	-189.4 ± 0.3	-187.0	-2.4	[2]
		(B) Chlorine Compounds				
1	Carbon tetrachloride	-30.7 ± 0.5	-22.9 ± 0.5	-22.9	0.0	[16]
2	Chloroform	-32.1 ± 0.3	-24.8 ± 0.4	-24.8	0.0	[16]
3	Dichloromethane	-29.8 ± 0.4	-23.0 ± 0.5	-23.0	0.0	[16]
4	Methyl chloride	-19.6 ± 0.2(g)	-19.6 ± 0.2	-21.8	+2.2	[17]
5	Tetrachloroethylene	-12.2 ± 2.0	-2.7 ± 1.0	-2.7	0.0	[2]
6	Trichloroethylene	-10.5 ± 1.6	-2.0 ± 1.6	-2.3	+0.3	[2]
7	1,1-Dichloroethylene	-5.7 ± 0.4	0.6 ± 0.4	0.6	0.0	[2]
8	1,2-Dichloroethylene, cis	-6.4 ± 2.0	1.0 ± 2.1	1.1	-0.1	[2]
9	1,2-Dichloroethylene, trans	-5.8 ± 2.0	1.2 ± 2.1	1.1	+0.1	[2]
10	Vinyl chloride	5.2 ± 0.5(g)	5.2 ± 0.5	5.3	-0.1	[15, 18]
11	1,1,1-Trichloroethane	-42.7 ± 0.3	-35.0 ± 0.5	-35.5	+0.5	[19, 20]
12	1,1-Dichloroethane	-39.5 ± 0.3	-31.0 ± 0.3	-31.1	+0.1	[4, 21]

continued

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(x)^a$ exptl (kcal/mole)	$\Delta H_f^\circ(g)^b$ obs (kcal/mole)	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Error^c (obs-calc) (kcal/mole)	Refs.^{d}
13	1,2-Dichloroethane	-40.6 ± 0.5	-32.1 ± 0.5	-32.9	+0.8	[16]
14	Poly(vinylidene chloride)	-24.0 ± 0.4(s)	(-18.5 ± 0.7)	-18.4	- 0.1	[15, 22]
15	Poly(vinyl chloride)	-22.6 ± 0.3(s)	(-18.4 ± 0.7)	-18.5	+0.1	[15, 22]
16	Ethyl chloride	-32.7 ± 0.4	-26.8 ± 0.2	-26.7	- 0.1	[2, 17]
17	1,2,3-Trichloropropene	-24.4 ± 0.5	(-14.2 ± 0.5)	-14.3	+0.1	[(16), 19]
18	2,3-Dichloropropene	-17.6 ± 0.5	(-10.3 ± 0.5)	-10.1	- 0.2	[16]
19	1,2,3-Trichloropropane	-55.7 ± 0.4	(-44.4 ± 0.6)	-46.6	(+2.2)	[4]
20	1,2-Dichloropropane	-48.2 ± 0.5	-39.6 ± 1.0)	-40.5	+0.9	[4]
21	1,3-Dichloropropane	-47.9 ± 2.0	-38.2 ± 2.0	-37.8	-0.4	[2]
22	2,2-Dichloropropane	-49.2 ± 2.0	(-41.4 ± 2.0)	-40.9	-0.5	[2]
23	1-Chloropropane	-38.6 ± 0.5	-31.7 ± 0.3	-31.6	-0.1	[17]
24	2-Chloropropane	-41.2 ± 0.5	-34.7 ± 0.3	-34.4	-0.3	[17, 20]
25	1-Chlorobutane	-43.0 ± 2.0	-35.2 ± 2.0	-36.5	+1.3	[2, 4]
26	(±)-2-Chlorobutane	-46.1 ± 2.0	-38.6 ± 2.0	-39.6	+1.0	[2, 4]
27	1-Chloro-2-methylpropane	-45.7 ± 2.0	-38.1 ± 2.0	-38.0	-0.1	[2, 4]
28	2-Chloro-2-methylpropane	-50.6 ± 0.6	-43.8 ± 0.6	-44.1	+0.3	[2,4]

29	1-Chloropentane	-50.7 ± 0.9	-41.6 ± 1.0	-41.4	-0.2	[2, 4]
30	1-Chloro-3-methylbutane	-51.7 ± 2.0	(-42.9 ± 2.0)	-42.9	0.0	[2]
31	2-Chloro-2-methylbutane	-56.4 ± 2.0	-48.4 ± 2.0	-48.1	-0.3	[2, 4]
32	2-Chlorohexane	-58.8 ± 0.4	(-49.2 ± 0.5)	-49.4	+0.2	[2]
33	Hexachlorobenzene	-30.6 ± 1.0(c)	-8.6 ± 2.3	-9.1	+0.5	[2]
34	1,2,4,5-Tetrachloro-dimethyl benzene	-41.5 ± 0.2(c)	(-20.0 ± 1.0)	-19.5	-0.5	[2, 16]
35	1,3-Dichlorobenzene	-5.0 ± 0.3	6.1 ± 0.5	5.9	+0.2	[2]
36	1,4-Dichlorobenzene	-10.4 ± 0.3(c)	5.5 ± 0.5	5.9	-0.4	[2, 4]
37	Chlorobenzene	2.6 ± 0.2	12.2 ± 0.4	12.3	-0.1	[2, 4]
38	Chlorocyclohexane	-49.5 ± 0.4	(-39.1 ± 0.8)	-39.2	+0.1	[2]
39	Benzyl chloride	-7.8 ± 0.6	(4.5 ± 0.6)	5.7	-1.2	[2, 16]
40	2,5-Dichlorostyrene	8.6 ± 0.5	(25.6 ± 1.0)	25.5	+0.1	[2]
	<u>Standard deviation</u>		±0.9		±0.6	
	<u>Exceptional cases</u>					
41	Hexachloroethane	-48.6 ± 1.3(c)	-34.5 ± 1.0	-39.5	+5.0	[2]
42	Pentachloroethane	-45.0 ± 1.6	-34.1 ± 1.7	-38.7	+4.6	[2]
43	1,1,2,2-Tetrachloro-ethane	-46.7 ± 1.4	-35.9 ± 1.5	-36.9	+1.0	[2]
44	1,2,2,3-Tetrachloro-propane	-60.3 ± 0.5	(-47.7 ± 1.0)	-48.4	+0.7	[16]

continued

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(x)^a$ exptl (kcal/mole)	$\Delta H_f^\circ(g)^b$ obs (kcal/mole)	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Error[c] (obs-calc) (kcal/mole)	Refs.[d]
45	α-Hexachlorocyclohexane	-41.2 ± 0.4(c)	-19.0 ± 1.0	-87.7	+68.7	[4, 23]
46	β-Hexachlorocyclohexane	-43.0 ± 0.4(c)	-18.4 ± 1.0	-87.7	+69.3	[4, 23]
47	γ-Hexachlorocyclohexane	-37.9 ± 0.4(c)	-10.3 ± 1.0	-87.7	+77.4	[4, 23]
48	δ-Hexachlorocyclohexane	-41.0 ± 0.4(c)	-17.7 ± 1.0	-87.7	+70.0	[4, 23]
49	α-Chloroethylbenzene	-13.9 ± 0.5	(-0.8 ± 1.0)	0.8	-1.6	[16]
50	β-Chloroethylbenzene	-2.5 ± 1.0	-2.5 ± 1.0	-2.7	+0.2	[24]
	(C) Bromine Compounds					
1	Methyl bromide	-14.6 ± 0.3	-9.1 ± 0.5	-10.9	(+1.8)	[2, 4]
2	Ethyl bromide	-21.9 ± 0.5	(-15.3 ± 0.5)	-15.9	(+0.6)	[2, 4]
3	1-Bromopropane	-28.3 ± 1.0	-20.7 ± 1.0	-20.7	0.0	[(2, 4)]
4	2-Bromopropane	-30.4 ± 0.6	-23.3 ± 0.7	-23.5	+0.2	[(2, 4)]
5	1,2-Dibromobutane	-34.3 ± 1.0	-23.5 ± 1.0	-23.4	-0.1	[2]
6	2,3-Dibromobutane	-33.6 ± 0.6	-24.6 ± 0.6	-25.0	+0.4	[2, (4)]
7	1-Bromobutane	-34.4 ± 0.3	-25.6 ± 0.5	-25.6	0.0	[2]
8	(±)-2-Bromobutane	-37.0 ± 0.3	-28.7 ± 0.5	-28.2	-0.5	[(2), 4]
9	2-Bromo-2-methylpropane	-39.3 ± 0.4	-31.9 ± 0.5	-31.9	0.0	[2]

10	1-Bromopentane	-40.7 ± 0.4	-30.9 ± 0.5	-30.5	-0.4	[2, 4]
11	1-Bromohexane	-46.4 ± 0.4	-35.5 ± 0.5	-35.4	-0.1	[2]
12	1-Bromoheptane	-52.2 ± 0.4	-40.2 ± 0.5	-40.3	+0.1	[2]
13	1-Bromo-octane	-58.6 ± 0.6	(-45.4 ± 0.6)	-45.2	-0.2	[2]
14	Vinyl bromide	18.7 ± 0.6(g)	18.7 ± 0.6	18.7	0.0	[2, 4]
15	Bromobenzene	14.5 ± 1.0	25.2 ± 1.0	25.2	0.0	[2, 4]
16	Benzyl bromide	5.6 ± 1.8	16.9 ± 1.8	16.6	+0.3	[2]
	Standard deviation		±0.9		±0.7	
	Exceptional cases					
17	1,2-Dibromopropane	-17.4 ± 0.5(g)	-17.4 ± 0.5	-18.7	+1.3	[4]
18	2,3-Dibromo-2-methylbutane	-33.1 ± 1.0(g)	-33.1 ± 1.0	-31.5	-1.6	[(2, 4)]
19	1,2-Dibromocyclopentane	-24.4 ± 0.5	-13.0 ± 0.5	-15.6	+2.6	[2]
20	1,2-Dibromocyclooctane	-41.4 ± 0.5	-28.4 ± 0.5	-25.9	-2.5	[2]
21	3-Bromo-1-propene	3.0 ± 1.4	(10.9 ± 1.6)	-9.4	+1.5	[2, 4]
			(D) Iodine Compounds			
1	Methyl iodide	-3.3 ± 0.3(g)	3.4 ± 0.3	2.7	+0.7	[2, 4]
2	Diiodomethane	16.0 ± 1.0	(28.2 ± 1.0)	28.2	0.0	[4]
3	Triiodomethane	33.7 ± 1.0(c)	50.4 ± 1.0	50.4	+0.0	[4]
4	1,2-Diiodoethane	0.2 ± 1.1(c)	15.9 ± 1.1	16.0	-0.1	[4]

continued

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(x)^a$ exptl (kcal/mole)	$\Delta H_f^\circ(g)^b$ obs (kcal/mole)	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Error[c] (obs-calc) (kcal/mole)	Refs.[d]
5	Ethyl iodide	-9.6 ± 0.5	- 2.0 ± 0.5	- 2.2	+0.2	[2, 4]
6	1,2-Diiodopropane	8.5 ± 0.9(g)	8.5 ± 0.9	8.5	0.0	[2]
7	1-Iodopropane	-15.7 ± 1.8	-7.1 ± 1.8	-7.1	0.0	[2]
8	2-Iodopropane	-17.9 ± 1.5	-9.8 ± 1.5	-9.8	-0.0	[2]
9	1,2-Diiodobutane	2.9 ± 1.5(g)	2.9 ± 1.5	- 3.8	-0.9	[4]
10	2-Iodo-2-methyl-propane	-26.0 ± 0.6	-17.5 ± 0.6	-17.5	0.0	[(2, 4)]
11	3-Iodo-1-propene	13.7 ± 1.1	(22.8 ± 1.0)	22.9	-0.1	[2, 4]
12	Iodobenzene	27.7 ± 1.0	(39.1 ± 1.0)	39.5	-0.4	[2]
13	Iodocyclohexane	-24.4 ± 2.1	-13.1 ± 2.1	-14.0	+0.9	[(2)]
14	1,2-Diiodobenzene	44.7 ± 1.0	(60.2 ± 2.0)	59.2	+1.2	[2]
15	1,4-Diiodobenzene	38.4 ± 1.0(c)	(57.4 ± 2.0)	59.2	-1.8	[2]
16	2-Iodotoluene	18.7 ± 1.0	(31.7 ± 1.0)	31.6	+0.1	[2]
17	3-Iodotoluene	18.7 ± 1.0	(31.7 ± 1.0)	31.6	+0.1	[2]
18	1-Iodonaphthalene	38.6 ± 1.5	(55.9 ± 1.5)	55.6	+0.3	[2]
19	2-Iodonaphthalene	34.5 ± 1.5(c)	(56.2 ± 1.5)	55.6	+0.6	[2]
	Standard deviation		±1.4		± 0.7	

	Exceptional cases					
20	Benzyl iodide	15.0 ± 1.0	26.3 ± 1.4	30.1	-3.8	[(2)]
21	1,3-Diiodobenzene	44.8 ± 1.0(c)	(63.5 ± 2.0)	59.2	+4.3	[(2)]
22	4-Iodotoluene	16.1 ± 1.0	(29.1 ± 1.0)	31.6	-2.5	[(2)]
			(E) Mixed Halocarbons			
1	Trifluorochloromethane	-169.3 ± 1.0(g)	-169.3 ± 1.0	-169.3	0.0	[3]
2	Trifluorobromomethane	-155.0 ± 0.6(g)	-155.0 ± 0.6	-155.0	0.0	[2, 3]
3	Trifluoroiodomethane	-140.6 ± 0.8(g)	-140.6 ± 1.0	-140.6	0.0	[3]
4	Difluorodichloromethane	-114.8 ± 2.0(g)	-114.8 ± 2.0	-115.9	+1.1	[2]
5	Difluorochloromethane	-115.6 ± 1.4(g)	-115.6 ± 1.4	-116.1	+0.5	[2]
6	Fluorotrichloromethane		-70.0 ± 2.0	-69.0	-1.0	[3]
7	Chlorotrifluoroethylene	-125.0 ± 4.0(g)	-125.0 ± 4.0	-124.6	-0.4	[2]
8	1,1-Difluorodichloroethylene	-80.2 ± 1.0(g)	-80.2 ± 1.0	-80.1	-0.1	[3]
9	1,1-Difluorochloroethylene	-79.2 ± 1.5(g)	-79.2 ± 1.5	-78.1	-1.1	[3]
10	1,2-Dichlorotetrafluoroethane	-220.1 ± 0.9	-214.5 ± 1.0	-213.1	-1.4	[(2, 3)]
11	1,1,2-Trifluorotrichloroethane		-169.9 ± 4.0	-169.8	-0.1	[2, 3]
12	1,2-Dibromotetrafluoroethane	-189.0 ± 1.1(g)	-189.0 ± 1.1	-189.4	+0.4	[2]

continued

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(x)$[a] exptl (kcal/mole)	$\Delta H_f^\circ(g)$[b] obs (kcal/mole)	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Error[c] (obs-calc (kcal/mole)	Refs.[d]
13	1,2-Dibromotrifluoro-chloroethane	-149.0 ± 4.0(g)	-149.0 ± 4.0	-149.0	0.0	[2, 3]
14	1,1,2,2-Tetrafluoro-bromoethane	-199.6 ± 0.9(g)	-199.6 ± 0.9	-199.2	-0.4	[2]
15	1-Chloro-2-bromo-1,2,2-trifluoroethane		(-155.8 ± 5.0)	-157.0	+1.2	[2, 3]
16	1,1-Difluorotetrachloro-ethane	-121.1 ± 0.6(g)	-121.1 ± 0.6	-128.5	(+7.4)	[3]
17	1,1-Difluoro-2,2-dichloro-1-bromethane	-111.7 ± 3.0(g)	-111.7 ± 3.0	-116.0	(+4.3)	[3]
18	1,2-Dichloro-1,2-dibromoethane	-8.8 ± 2.1(g)	-8.8 ± 2.1	-25.1	(+16.3)	[2]
19	1,2-Dichlorohexafluoro-cyclobutane	-273.0 ± 2.0(g)	-273.0 ± 2.0	-281.6	(+8.6)	[3]
	<u>Standard deviation:</u>		±2.2		±0.7	

[a] x = phase; values for liquid phase, unless otherwise indicated.
g = gas, c = crystalline solid, s = amorphous solid.

[b] Figures in parenthesis based on calculated enthalpy of phase-change.

[c] Parenthesized figures are excluded from overall standard deviation.

[d] Parenthesized reference indicate recalculation or selection of experimental data by this author.

[e] An estimate from other empirical schemes.

Fluorine Compounds

The following points were noted when correlating fluorine compounds on the basis of the additivity principle.

1. The carbon-fluorine bond strength in perfluoroalkanes increased progressively with the number of fluorine substitutions on a single C^3-carbon. Four bond-energy terms (Nos. 1 to 4 in Table 2) were derived to account for this effect.
2. Progressive fluorine substitution in the benzene nucleus gave rise to a decreasing pattern of bond energies which was fitted to an empirical equation, No. 10 in Table 2. This equation indirectly takes care of the various dipole-dipole interactions of hydrogen and fluorine atoms on the aromatic nucleus, although much less rigorously than in the work of Cox et al. [25]. The subtle differences of ortho, meta, and para substitutions also remain beyond the scope of the empirical equation.
3. When dealing with partially fluorinated hydrocarbons containing both fluorine and hydrogen atoms in the molecule, it was noted that energy terms derived merely from perfluoro compounds substantially underestimated the binding energy, viz., the experimental $\Delta H_f^\circ(g)$ being more negative. Intramolecular hydrogen-fluorine bond-strengthening interactions (H-bonding or dipole-dipole) exerted a substantial influence on the overall heat of formation. These nonbonded interactions have been resolved in the present scheme, partly by envisaging three additional bond-energy terms (Nos. 5 to 7, Table 2) to be used when a fluorine atom is placed on the carbon atom already bonded to the hydrogen, and partly by generating two vicinal (1-2) interaction terms Nos. 11 and 12 in the same table.
4. The slightly larger fluorine atom (van der Waals radius, r = 1.35 Å) replacing hydrogen (r = 1.0 Å) does not lead to any significant steric hindrance in fluorocarbons as judged from molecular models. No special steric terms beyond those already evolved for hydrocarbons [1] seem necessary.

The bond-energy terms of Table 2 when applied to almost all the available data on fluorocarbons listed in Refs. 2-4 and 26 yield calculated values within standard deviation of ±0.7 kcal/mole, which is much less than the experimental uncertainty of ±1.2 kcal/mole associated with the data on fluorocarbons. Some of the outstanding cases of disagreement are 1,1,2-trifluoroethane ($\Delta\Delta = -5.4$) and trifluoromethylbenzene ($\Delta\Delta = 3.6$). No explanation is possible beyond attributing these differences (obs - calc) to very special fluorine-hydrogen nonbonded interactions permitted by the specific molecular conformation. Other exceptions such as perfluoroethane and perfluorocyclobutene can be attributed to steric effects due to the larger size of fluorine. However, the large positive deviation of over 12 kcal for perfluorobutadiene seems to be clearly due to the vanishing resonance energy in the $C^2—C^2$ bond of butadiene on perfluorination [27]. When more data on perfluorinated dienes, diynes, etc. become available, the bond-energy terms such as $C^2—C^2$, $C^2—C^\phi$, $C^1—C^2$, $C^1—C^\phi$, and $C^1—C^1$ may have to be revised for such conjugated perfluorocarbons.

Chlorine Compounds

The chlorine atom (r = 1.8 Å) has approximately the same size as the methyl group. Therefore the same steric interaction terms of the hindered alkanes in Part I [1a] have been employed, treating the chlorine atom as equivalent to a methyl group. Thus a $C^3—C^3$ carbon-carbon bond in chlorine compounds had various values ranging from +0.45 to +6.54 as given in Table 1. The heat of formation is also influenced by the 1-3 steric interaction, as for the hindered alkanes, especially polymers like polyisobutylene. All carbon-chlorine bond energy terms have been derived after taking into account these basal steric energy corrections due to the size of the chlorine atom. These correction terms are also applicable to bromine (r = 1.95 Å) and iodine (r = 2.15 Å) compounds, but with somewhat enhanced magnitudes which are at present unknown due to the lack of relevant thermochemical data. Further observations made on chlorine compounds are as follows:

1. Separate energy terms for primary, secondary, and tertiary singular chlorine substitution as well as different terms for the multiple substitution on a single carbon atom were found necessary as terms Nos. 13 to 18 in Table 2. Unlike fluorine, the multiple substitution reduces the carbon-chlorine bond strength progressively.
2. Progressive chlorine substitution in the benzene nucleus also decreases the C—Cl bond strength, which has been fitted to an empirical equation No. 21 in Table 2, similar to fluorine. This equation implicitely takes into account both the ortho-steric effect and the chlorine-hydrogen nonbonded interaction which are opposite in nature.
3. The major hydrogen-chlorine nonbonded interaction terms contributing to the total binding energy [negative $\Delta H_f^\circ(g)$] in certain chlorine compounds are worked out as terms Nos. 25 to 27 in Table 2, similar to fluorine but appreciably less in magnitude. Several other bond-strengthening interactions of this type (but with smaller magnitudes) were clearly perceptible in chlorine compounds when a particular placement of chlorine in the vicinity of hydrogens is responsible. However, no generalization on the basis of the additivity principle could be worked out.
4. The carbon-chlorine bond is apparently weakened when the carbon atom is already bonded to two or more fluorine atoms. Terms

Nos. 23 and 24 are prescribed for these bonds. Such an inductive influence of fluorine is very much pronounced in the case of bromine and iodine bonds with fluorine-bonded carbon.

5. Of the exceptional cases of disagreement (41 to 49, Table 3B), compounds Nos. 41 to 44 are clearly attributable to the steric crowding of chlorine atoms in heavily chlorinated alkanes and perchloroalkanes for which the present scheme, which treats the steric effects of chlorine atom as equivalent to a methyl group, is clearly inadequate. Hexachlorocyclohexane isomers (compounds Nos. 45 to 48), with their extraordinary steric instability of the order of 68 to 77 kcal/mole, also point out the inapplicability of the bond-additivity principle to cyclic compounds, especially the halogenated ones.

Bromine and Iodine Compounds

The available experimental data does not permit assessment of the steric factors which are involved in the multiple substitution of bromine on a single carbon atom. All other possible energy terms have been evaluated on the same lines as for fluorine and chlorine compounds, as listed in Table 2. Carbon-bromine and carbon-iodine bonds are relatively insensitive to the typical variations of the carbon atom.

Mixed Halocarbons and the Key-Data

When fluorine is present on a carbon atom, the bond strength of other halogen bonds on the same carbon is substantially reduced, especially for bromine and iodine bonds, as seen from the energy terms Nos. 23, 24, 33, 34, and 41 in Table 2, which have been derived on the basis of experimental data from Table 3 (E). Bond energy terms for several halogen bonds other than between carbon and halogen are given at the end of Table 2. These have been derived from appropriate data on key compounds of the halogen thermochemistry. Such key data are extremely precise and well confirmed by thermochemists all over the world [7] as the reference point for the bonding energy in chemical compounds.

DISCUSSION

One of the simplest applications of thermochemical data to heats of formation is the prediction of the heat of a chemical reaction. Heats of polymerization, $\Delta H_p^\circ(gg)$, are predicted in Table 4 and compared, wherever possible, with the experimental data on heats of polymerization with, however, different phases of monomers and polymers. It is

TABLE 4. Heats of Formation and Polymerization of Halogen-Containing Monomer-Polymer Systems

					Heat of polymerization		
System no.	Monomer	$\Delta H_f^\circ(g)$ calc (kcal/mole)	Polymer	$\Delta H_f^\circ(g)$ calc (kcal/mole)	$-\Delta H_p^\circ(gg)$ calc (kcal/mole)	$-\Delta H_p^\circ(xy)$ obs (kcal/mole)	Refs.
1	Tetrafluoroethylene	-157.4	Poly(tetrafluoroethylene)	-194.3	36.9	41.7(gc)	[28]
2	Trifluoroethylene	-117.5	Poly(trifluoroethylene)	-150.0	32.5		
3	Vinylidene fluoride	-82.5	Poly(vinylidene fluoride)	-110.5	28.0	33.6(gs)	[28]
4	Vinyl fluoride	-32.6	Poly(vinyl fluoride)	-53.9	21.3		
5	Chlorotrifluoroethylene	-124.6	Poly(chlorotrifluoroethylene)	-155.0	30.4		
6	Dichlorodifluoroethylene	-80.1	Poly(dichlorodifluoroethylene)	-107.4	27.3		
7	Vinylidene chloride	+0.6	Poly(vinylidene chloride)	-18.4	19.0	17.7(ls)	[28]
8	Vinyl chloride	+5.3	Poly(vinyl chloride)	-18.5	23.8	22.9(ls)	[28]
9	Allyl chloride	-1.5	Poly(allyl chloride)	-22.0	20.5	18.5(ls)	[29]

10	2,3-Dichloropropene	-10.1	Poly(2,3-dichloropropene)	-27.0	16.9		
11	1,2,3-Trichloropropene	-14.3	Poly(1,2,3-trichloropropene)	-31.2	16.8		
12	Chloroprene	+19.1	1,4-cis Poly(chloroprene)	+1.9	17.2	16.2(ls)	[28]
			1,4-trans Poly (chloroprene	+1.0	18.1		
13	α-Chlorostyrene	+28.3	Poly(α-chlorostyrene)	+10.8	17.5		
14	p-Chlorostyrene	+27.9	Poly(p-chlorostyrene)	+9.0	18.9	16.0(1s)	[28]
15	2,5-Dichlorostyrene	+21.8	Poly(2,5-dichlorostyrene)	+2.5	19.3	16.5(ls)	[28]
16	Difluoroacetylene ($CF\equiv CF$)[a]	-26.6	Poly(carbon monofluoride):				
			(a) linear, $-(CF=CF)-$	-65.4[b]	38.8(gg)	-89.3[c]	[29]
			(b) cross-linked, $>(CF-CF)<$	-90.1	63.5(gg)		
17	$-(C_2H_4)_2- \quad +Cl_2(g)$ $-(C_2H_4)_3- \quad +Cl_2(g)$ HCl(g) + polymer		Chlorinated polyethylene:				
			$-(C_4H_7Cl)-$, 40% chlorine	-28.4	30.8	Heat of chlorination per random chlorine substitution	
			$-(C_6H_{11}Cl)-$, 30% chlorine	-38.2			

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[a] Hypothetically taken as the monomer and $\Delta H_f^\circ(g)$ calculated assuming C^1-F = -55.8, the highest value (Table 2) recorded for the C—F bond.

[b] Assuming no resonance energy for the C^2-C^2 bond as in perfluorobutadiene (Table 3, A-31).

[c] Experimental value [29] of ΔH_f°(polymer,g), using the same heat of sublimation as for Teflon [15].

contended that the bond energy scheme presented here renders general experimental combustion calorimetric work on polymers [30] unnecessary, unless performed with high precision [11] for the special purpose of evaluating conformational energies due to stereospecificity.

Experimental heats of polymerization of fluoroethylenes measured directly in a polymerization calorimeter have not yet become available, and only combustion data for Teflon and poly(vinylidene fluoride) polymers and the respective monomers are available. When appropriate enthalpies of phase changes are taken into account for the polymers, the calculated (hypothetical) values of $\Delta H^\circ_p(gg)$ agree with the bond energy scheme within the precision of experimental calorimetry. In view of recent interest in poly(carbon monofluoride), $(CF)_x$ [29], as a new polymer in space technology [31], we attempted to assign two possible structures to this polymer as in Table 4. It appears that the cross-linked structure is closer energetically to the experimental heat of formation [29], assuming that the carbon-fluorine bond is "normal." The cross-linked structure is also in harmony with the insoluble, infusible nature and extraordinary thermal stability at 600°C of this novel Teflon-analog, for which the only technical use envisaged at present is a solid lubricant superior to graphite.

REFERENCES

[1] R. M. Joshi, J. Macromol. Sci.—Chem., (a) A4(8), 1819 (1970); (b) A5(4), 687 (1971); A6(3), 595 (1972).

[2] J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic, London, 1970.

[3] J. R. Lacher and H. A. Skinner, J. Chem. Soc., A, 1968, 1034.

[4] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamic Properties of Organic Compounds, Wiley, New York, 1969.

[5] G. T. Armstrong, Nat. Bur. Stand., Tech. Note 513, 1970.

[6] V. H. Diebeler, J. A. Walker, and K. E. McCulloh, J. Chem. Phys., 51, 4230 (1969); 50, 4592 (1969).

[7] ICSU-CODATA Task Group, J. Chem. Thermodyn., 4(3), 331 (1972).

[8] R. C. King and G. T. Armstrong, J. Res. Nat. Bur. Stand., A, 74(6), 769 (1970).

[9] A. P. Kudchadkar, S. A. Kudchadkar, and P. M. Agarwal, Ind. J. Chem., 9(7), 722 (1971).

[10] D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed. (NSRDS-NBS 37), National Bureau of Standards, Washington, D.C., 1971.

[11] R. M. Joshi and B. J. Zwolinski, Macromolecules, 1, 25 (1968).

[12] W. D. Good, D. W. Scott, and G. Waddington, J. Phys. Chem., 60, 1080 (1956).

[13] J. L. Wood, R. J. Lagow, and J. L. Margrave, J. Chem. Eng. Data, 12, 225 (1967).

[14] E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Stand., A, 69, 137 (1965).

[15] R. M. Joshi, "Thermodynamic Properties," in Encyclopedia of Polymer Science and Technology, Vol. 13 (H. Mark, N. G. Gaylord, and N. Bikales, eds.), Wiley (Interscience), New York, 1970, pp. 788-831.

[16] A. T. Hue and G. C. Sinke, J. Chem. Thermodyn., 1(6), 507 (1969).

[17] R. A. Fletcher and G. Pilcher, Trans. Faraday Soc., 67(II), 3191 (1971).

[18] R. M. Joshi, J. Polymer Sci., B, 3,779 (1965).

[19] A. T. Hue, G. C. Sinke, and M. J. Mintz, J. Chem. Thermodyn., 4(2), 239 (1972).

[20] I. Noren and S. Sunner, Ibid., 2(4), 597 (1970).

[21] M. Mansson, B. Ringner, and S. Sunner, Ibid., 3(4), 547 (1971).

[22] G. C. Sinke and D. R. Stull, J. Phys. Chem., 62, 397 (1958).

[23] A. H. Jones, J. Chem. Eng. Data, 5(2), 196 (1960).

[24] R. M. Joshi, Unpublished Results, gas-phase reaction (2nd law), of styrene and hydrochloric acid.

[25] J. D. Cox, H. A. Gundry, and A. J. Head, Trans. Faraday Soc., 60, 653 (1964).

[26] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Revs., 69, 279 (1969).

[27] C. R. Patrick, in Advances in Fluorine Chemistry, Vol. 2 (M. Stacey, J. C. Tatlow and A. G. Sharpe, eds.), Academic, New York, 1961, pp. 1-34.

[28] R. M. Joshi and B. J. Zwolinski, in Vinyl Polymerization, Vol. 1, Pt. 1 (G. E. Ham, ed.), Dekker, New York, 1967, Chap. 8.

[29] J. L. Wood, R. B. Badachhape, R. J. Lagow, and J. L. Margrave, J. Phys. Chem., 73(9), 3139 (1969).

[30] J. Franz, W. Mische, and P. Kuzay, Plaste Kaut., 14(7), 472 (1967); K. Krekeler and P. M. Klimke, Kunstoffe, 55(10), 758 (1965).

[31] American Chemical Society Note, Chem. Eng. News, April 23, 1973, p. 37.

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