

and water.

TABLE 2.2  
Standard molar enthalpies of formation, 298.15 K

Compound <sup>a</sup>	$\Delta_f H^\circ(\text{g})/\text{kJ mol}^{-1}$	Compound	$\Delta_f H^\circ(\text{g})/\text{kJ mol}^{-1}$
HF	-273.30	NO <sup>b</sup>	+90.29
HCl	-92.31	ICl <sup>b</sup>	+17.51
HBr	-36.38	CH <sub>4</sub> <sup>b</sup>	-74.873
HI	+26.36	CH <sub>3</sub> F <sup>b</sup>	-234
CO	-110.53	CH <sub>3</sub> Cl <sup>b</sup>	-86.44
H <sub>2</sub> O <sup>d</sup>	-241.814	CH <sub>3</sub> Br <sup>c</sup>	-38
CO <sub>2</sub>	-393.51	CH <sub>3</sub> I <sup>c</sup>	+14
SO <sub>2</sub>	-296.81	CH <sub>3</sub> OH <sup>c</sup>	-201.1
NH <sub>3</sub>	-45.94	CF <sub>4</sub> <sup>c</sup>	-934.3
BF <sub>3</sub>	-1135.95	HC≡CH <sup>b</sup>	+226.7
SiF <sub>4</sub>	-1614.95	H <sub>2</sub> C=CH <sub>2</sub> <sup>b</sup>	+52.47
		C <sub>2</sub> H <sub>6</sub> <sup>c</sup>	-84.68
		C <sub>3</sub> H <sub>8</sub> <sup>c</sup>	-103.9
		C <sub>6</sub> H <sub>6</sub> <sup>c,d</sup>	+82.89
		CH <sub>3</sub> NH <sub>2</sub> <sup>c</sup>	-23.0
		Cyclopropane <sup>c</sup>	+53.3
		Cyclobutane <sup>c</sup>	+28.4
		Cyclopentane <sup>c</sup>	-77.15
		Cyclohexane <sup>c,d</sup>	-123.4

<sup>a</sup> Ref. 4. <sup>b</sup> Ref. 5. <sup>c</sup> Ref. 1. <sup>d</sup>  $\Delta_f H^\circ(\text{l})$  may be obtained from  $\Delta_f H^\circ(\text{g})$  given here and  $\Delta_v H^\circ_{298\text{K}}$  from Table 2.1, p. 49.

TABLE 2.3  
Standard bond dissociation enthalpies of some gaseous diatomic elements and compounds, 298.15 K<sup>a</sup>

Element(g)	$DH^\circ/\text{kJ mol}^{-1}$	Compound(g)	$DH^\circ/\text{kJ mol}^{-1}$
H <sub>2</sub>	435.99	HF	570.7
N <sub>2</sub>	945.36	HCl	431.6
O <sub>2</sub>	498.34	HBr	366.2
F <sub>2</sub>	158.8	HI	298.4
Cl <sub>2</sub>	242.60	CO	1076.4
Br <sub>2</sub>	192.8	NO	631.6
I <sub>2</sub>	151.10	ICl	210.6

<sup>a</sup> The values for the elements were obtained from spectroscopic results.<sup>4</sup> Those for the heteronuclear diatomics were calculated from

$$DH^\circ(\text{AB}) = \Delta_f H^\circ(\text{A, g}) + \Delta_f H^\circ(\text{B, g}) - \Delta_f H^\circ(\text{AB, g});$$

$\Delta_f H^\circ$  data for compounds are given in Table 2.2 (p. 52) and for atomic elements in Table 2.4 (p. 59).

TABLE 2.4  
Standard molar enthalpies of formation of atoms and free radicals,  
298.15 K

Atom <sup>a</sup>	$\Delta_f H^\circ(\text{g})/\text{kJ mol}^{-1}$	Radical	$\Delta_f H^\circ(\text{g})/\text{kJ mol}^{-1}$
H	217.997	CH <sub>3</sub>	145.7 <sup>b</sup>
B	560	CH <sub>2</sub>	385.2 <sup>b</sup>
C	716.67	CH	594.1 <sup>b</sup>
N	472.68	C <sub>2</sub> H <sub>5</sub>	105 <sup>c</sup>
O	249.17	n-C <sub>3</sub> H <sub>7</sub>	95 <sup>c</sup>
S	276.98	(CH <sub>3</sub> ) <sub>2</sub> CH	74 <sup>c</sup>
Si	450	(CH <sub>3</sub> ) <sub>3</sub> C	34 <sup>c</sup>
F	79.39	C <sub>6</sub> H <sub>5</sub>	325 <sup>d</sup>
Cl	121.302	OH	39.46 <sup>b</sup>
Br	111.86	NH	339 <sup>b</sup>
I	106.762	NH <sub>2</sub>	168 <sup>b</sup>

<sup>a</sup> Ref. 4. <sup>b</sup> Ref. 5. <sup>c</sup> Ref. 10. <sup>d</sup> G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.* **67**, 2077 (1971).

TABLE 2.5  
Standard dissociation enthalpies ( $DH^\circ$ ) for bonds in simple polyatomic compounds,  
298.15 K

Compound-bond	$DH^\circ/\text{kJ mol}^{-1}$	Compound-bond	$DH^\circ/\text{kJ mol}^{-1}$
CH <sub>3</sub> -F	459 <sup>a</sup>	CH <sub>3</sub> -H	438.6 <sup>a</sup>
CH <sub>3</sub> -Cl	353.4 <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> -H	408 <sup>d</sup>
CH <sub>3</sub> -Br	296 <sup>a</sup>	(CH <sub>3</sub> ) <sub>2</sub> CH-H	396 <sup>d</sup>
CH <sub>3</sub> -I	238 <sup>a</sup>	(CH <sub>3</sub> ) <sub>3</sub> C-H	387 <sup>d</sup>
CH <sub>3</sub> -NH <sub>2</sub>	331 <sup>b</sup>	PhCH <sub>2</sub> -H	355 <sup>d</sup>
CH <sub>3</sub> -OH	381 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub>	418 <sup>c</sup>
CH <sub>3</sub> -OCH <sub>3</sub>	335 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub>	389 <sup>c</sup>
HO-H	499.3 <sup>a</sup>	CH <sub>3</sub> -CH <sub>3</sub>	376.1 <sup>c</sup>
CH <sub>3</sub> O-H	427 <sup>b</sup>	(CH <sub>3</sub> ) <sub>3</sub> C-CH <sub>3</sub>	335 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> O-H	356 <sup>c</sup>	(CH <sub>3</sub> ) <sub>3</sub> C-C(CH <sub>3</sub> ) <sub>3</sub>	282 <sup>c</sup>

<sup>a</sup> From data in Tables 2.2 and 2.4; see p. 58 for the example of CH<sub>3</sub>Cl.  
<sup>b</sup> Ref. 8. <sup>c</sup> Ref. 6. <sup>d</sup> Ref. 10. <sup>e</sup> Calculated on p. 58.

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CH<sub>3</sub>-Cl)

(CH<sub>3</sub>Cl)

single atom. The  
I<sub>3</sub>-CH<sub>3</sub>) from

-CH<sub>3</sub>)

I<sub>6</sub>, g)

Table 2.8 BOND DISSOCIATION ENERGIES AND AVERAGE BOND ENERGIES FOR VARIOUS TYPES OF BONDS (kcal mole<sup>-1</sup>)

Bond Dissociation Energies<sup>a</sup>—Single Bonds: Diatomic Molecules

Bond	Energy	Bond	Energy	Bond	Energy
H—H	104.2	F—Cl	61	H—F	135.8 <sup>b</sup>
D—D	106.0	F—Br	60	H—Cl	103.0 <sup>b</sup>
F—F	38	F—I	58	H—Br	87.5 <sup>b</sup>
Cl—Cl	58	Cl—Br	52	H—I	71.3 <sup>b</sup>
Br—Br	46.0	Cl—I	50		
I—I	36.1				

Polyatomic Molecules

Bond	Energy	Bond	Energy	Bond	Energy
H—CH <sub>3</sub>	104	Cl—CCl <sub>3</sub>	73	H—OH	119
H—CH <sub>2</sub> CH <sub>3</sub>	98	Br—CCl <sub>3</sub>	54	H—O <sub>2</sub> H	90
H—CHCH <sub>2</sub>	103	F—COCH <sub>3</sub>	119	H—SH	90
H—C <sub>6</sub> H <sub>5</sub>	103	Cl—COCH <sub>3</sub>	83.5	H—OCH <sub>3</sub>	102
H—CCH	~125	I—COCH <sub>3</sub>	52.5	H—OC <sub>6</sub> H <sub>5</sub>	85
H—CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	85			H—O <sub>2</sub> CCH <sub>3</sub>	112
H—CH <sub>2</sub> CHCH <sub>2</sub>	85	CH <sub>3</sub> —CH <sub>3</sub>	88		
H—CH <sub>2</sub> OH	93	CH <sub>3</sub> —CH <sub>2</sub> CH <sub>3</sub>	85	HO—CH <sub>3</sub>	91.5
H—CF <sub>3</sub>	104	CH <sub>3</sub> —CH <sub>2</sub> OH	83	HO—CH <sub>2</sub> CH <sub>3</sub>	91.5
H—CCl <sub>3</sub>	96	CH <sub>3</sub> —CF <sub>3</sub>	100	HO—C <sub>6</sub> H <sub>5</sub>	103
H—COCH <sub>3</sub>	87.5	CH <sub>3</sub> —CHCH <sub>2</sub>	92	HO—COCH <sub>3</sub>	109
H—CN	130	CH <sub>3</sub> —C <sub>6</sub> H <sub>5</sub>	93		
		CH <sub>3</sub> —CCH	117	CH <sub>3</sub> O—CH <sub>3</sub>	80
F—CH <sub>3</sub>	108	CH <sub>3</sub> —CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	72	CH <sub>3</sub> O—CH <sub>2</sub> CH <sub>3</sub>	80
Cl—CH <sub>3</sub>	83.5	CH <sub>3</sub> —CH <sub>2</sub> CHCH <sub>2</sub>	72	CH <sub>3</sub> O—CHCH <sub>2</sub>	87
Br—CH <sub>3</sub>	70	CH <sub>3</sub> CH <sub>2</sub> —CHCH <sub>2</sub>	89	CH <sub>3</sub> O—C <sub>6</sub> H <sub>5</sub>	91
I—CH <sub>3</sub>	56	CH <sub>3</sub> CH <sub>2</sub> —C <sub>6</sub> H <sub>5</sub>	90	CH <sub>3</sub> O—COCH <sub>3</sub>	97
F—CH <sub>2</sub> CH <sub>3</sub>	106	CH <sub>2</sub> CH—CHCH <sub>2</sub>	100		
Cl—CH <sub>2</sub> CH <sub>3</sub>	81.5	HCC—CCH	150	HO—OH	51
Br—CH <sub>2</sub> CH <sub>3</sub>	69	C <sub>6</sub> H <sub>5</sub> —C <sub>6</sub> H <sub>5</sub>	100	HO—Br	57
I—CH <sub>2</sub> CH <sub>3</sub>	53.5	CH <sub>2</sub> CH—C <sub>6</sub> H <sub>5</sub>	99	CH <sub>3</sub> O—OCH <sub>3</sub>	36
Cl—CHCH <sub>2</sub>	84				
F—C <sub>6</sub> H <sub>5</sub>	116	CH <sub>3</sub> —COCH <sub>3</sub>	82	H <sub>2</sub> N—H	103
Br—C <sub>6</sub> H <sub>5</sub>	72	CH <sub>3</sub> CH <sub>2</sub> —COCH <sub>3</sub>	79	H <sub>2</sub> N—CH <sub>3</sub>	79
I—C <sub>6</sub> H <sub>5</sub>	65	CH <sub>3</sub> —CN	122	H <sub>2</sub> N—CH <sub>2</sub> CH <sub>3</sub>	78
F—CF <sub>3</sub>	129	CH <sub>2</sub> CH—COCH <sub>3</sub>	89	H <sub>2</sub> N—C <sub>6</sub> H <sub>5</sub>	91
Cl—CF <sub>3</sub>	85	CH <sub>2</sub> CH—CN	128	H <sub>2</sub> N—COCH <sub>3</sub>	~96
Br—CF <sub>3</sub>	70	CH <sub>3</sub> CO—COCH <sub>3</sub>	83		
I—CF <sub>3</sub>	54	NC—CN	144	O <sub>2</sub> N—NO <sub>2</sub>	13.6
F—CCl <sub>3</sub>	106	CF <sub>3</sub> —CF <sub>3</sub>	97	O <sub>2</sub> N—COCH <sub>3</sub>	97

Multiple Bonds

Bond	Energy	Bond	Energy
O=O	119	CF <sub>2</sub> =CF <sub>2</sub>	76.3
O=CO	128	CH <sub>2</sub> =NH	~154
O=CH <sub>2</sub>	175	C≡O	257
O=NH	115	N≡N	226
HN=NH	~109	N≡CH	224
CH <sub>2</sub> =CH <sub>2</sub>	163	HC≡CH	230

1 wt = 4.184 J

Table 2.8 (Continued)

Representative Average Bond Energies <sup>c</sup> —Single Bonds								
	C	N	O	F	Cl	Br	I	Si
H	100	93	110	136	103	88	71	72
C	81	69	84	105	79	67	57	69
N		38	43	65	48			
O			33	50	50	53	57	103
F					60	60	67	141
Cl						53	50	96
Br							43	69
I								50
Si								45

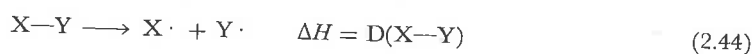
Multiple Bonds			
Elements	Single bond	Double bond	Triple bond
O—O	33	96	
N—N	38	100	226
C—C	81	148	194
C—O	84	172	
C—N	69	148	213

<sup>a</sup>From A. J. Gordon and R. A. Ford, *The Chemists Companion*, Wiley, New York, 1972. Reprinted by permission of John Wiley & Sons, Inc.

<sup>b</sup>S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965). Reprinted by permission of the Division of Chemical Education.

<sup>c</sup>From J. Waser, K. N. Trueblood, and C. M. Knobler, *Chem One*, McGraw-Hill, New York, 1976. Adapted by permission of McGraw-Hill.

energies; that is, the enthalpy change of the reaction:



Bond dissociation energies are useful for simple reactions, particularly of the free-radical type, in which one or two single bonds are formed or broken. Energy changes in more complex reactions may be approximated using the averaged bond energies given at the end of the table. The sum of the averaged bond energies of a molecule represents the enthalpy of its formation from its constituent atoms. The averaging is necessary because successive breaking of the bonds of a given type in a molecule requires different amounts of energy for each bond.

More accurate estimates of reaction thermochemistry may be obtained by the use of Benson's additivity rules, which allow calculation of  $\Delta H_f^\circ$  and  $S^\circ$  for molecules in the gas phase. When an accurate experimental value is known, the calculated value is almost always within a few tenths of a kilocalorie of it, and usually the agreement is even better.

Benson's approach is to determine the  $\Delta H_f^\circ$  of a molecule by adding together the  $\Delta H_f^\circ$ 's of the various groups in the molecule. A group is defined as an atom and its ligands. For example,  $\text{CH}_3\text{CH}_3$  is made up of two identical groups.