Enthalpy of Combustion, Bond Enthalpy, Spontaneous and Non-Spontaneous Processes

Learning Objective	Openstax 2e Chapter
Thermochemistry of Combustion	<u>5.3</u>
Bond Energy and Enthalpy	ŧ
Introduction to Spontaneity	<u>16.1</u>

†See the complementary e-textbook:

• First Year General Chemistry by Mombourquette, Chapter 7.6

Suggested Practice Problems

<u>Chapter 5 Exercises</u> – Questions: 45*, 49, 51*, 57*, 73*, 79, 81

Answers can be found in the **Chapter 5 Answer Key**

*Use Appendix G for standard enthalpies of formation to calculate ΔH

TABLE 7.4 Approximate Heats of Combustion of Some Fuels

Heat of Combustion

Fuel	kJ/g
Municipal waste	-12.7
Cellulose	-17.5
Pinewood	-21.2
Methanol	-22.7
Peat	-20.8
Bituminous coal	-28.3
Isooctane	-47.8
(a component	
of gasoline)	
Natural gas	-49.5

Example 1: Determine the standard enthalpy of combustion for methane.

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(I)$$
Reactant(s)

Product(s)

TABLE 7.2 So $\Delta_f H^\circ$ at 298.15		Enthalpies of Forma	tion,
Substance	kJ/mol ^a	Substance	kJ/mol ^a
CO(g)	-110.5	HBr(g)	-36.40
$CO_2(g)$	-393.5	HI(g)	26.48
$CH_4(g)$	-74.81	$H_2O(g)$	-241.8
$C_2H_2(g)$	226.7	$H_2O(1)$	-285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	-20.63
$C_2H_6(g)$	-84.68	$NH_3(g)$	-46.11
$C_3H_8(g)$	-103.8	NO(g)	90.25
$C_4H_{10}(g)$	-125.6	$N_2O(g)$	82.05
$CH_3OH(1)$	-238.7	$NO_2(g)$	33.18
$C_2H_5OH(1)$	-277.7	$N_2O_4(g)$	9.16
HF(g)	-271.1	$SO_2(g)$	-296.8
HCl(g)	-92.31	SO ₃ (g)	-395.7

^aValues are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Solution:

$$\Delta_r H^{\circ} = [\mathbf{1} \Delta_f H^{\circ}(CO_2) + \mathbf{2} \Delta_f H^{\circ}(H_2O)] - [\mathbf{1} \Delta_f H^{\circ}(CH_4) + \mathbf{2} \Delta_f H^{\circ}(O_2)]$$

$$= [\mathbf{1} \times (-393.5) + \mathbf{2} \times (-285.8)] - [\mathbf{1} \times -74.81 + \mathbf{2} \times 0]$$

$$= -890.3 \text{ kJ/mol}$$

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Average Bond Enthalpies (BE)

BE can be considered as the "energy" required to break one mole of the chemical bond. We can use BE to estimate $\Delta_r H^0$. Note that:

- Average bond enthalpies are all positive!
- These are <u>average</u> bond enthalpies; the C—H bonds in methane, CH₄, will be a bit different than the C—H bond in chloroform, CHCl₃.
- Bond forming reaction is exothermic

$$2Cl(g) \rightarrow Cl_2(g)$$
 $\Delta_r H^o = -242 \text{ kJ/mol}$

Bond breaking reaction is endothermic

$$Cl_2(g) \rightarrow 2Cl(g)$$
 $\Delta_r H^o = +242 \text{ kJ/mol}$

Table of average bond enthalpies (kJ/mol)

Single B	Sonds						
С—Н	413	N-H	391	О-Н	463	F-F	155
C-C	348	N-N	163	0-0	146	C1 F	252
C-N	293	N-O	201	O-F	190	Cl—F	253
c-o	358	N-F	272	O-C1	203	Cl-Cl	242
C-F	485	N-C1	200	O-I	234		
C-C1	328	N-Br	243			Br—F	237
C-Br	276			S-H	339	Br-Cl	218
C-I	240	H-H	436	S-F	327	Br—Br	193
C-S	259	H-F	567	S-C1	253		
		H-Cl	431	S—Br	218	I-Cl	208
Si—H	323	H-Br	366	S-S	266	I—Br	175
Si—Si	226	H-I	299			I-I	151
Si-C	301						
Si-O	368						
Si—Cl	464						
Multiple	e Bonds						
C = C	614	N=N	418	O_2	495		
$C \equiv C$	839	$N \equiv N$	941				
C=N	615	N=0	607	s=0	523		
$C \equiv N$	891	ser4.39 1005.3	Hardware PROCEST	s=s	418		
C=O	799				contractor Total es Ta les		
C≡O	1072						

Now we can use average bond enthalpies to <u>estimate</u> enthalpy of reaction $(\Delta_r H^\circ)$

Estimate $\Delta_r H^o$ for the reaction:

average bond enthalpies (kJ/mol) Single Bonds

$$CH_4(g) + CI_2(g) \rightarrow CH_3CI(g) + HCI(g)$$

$$\Delta_r H^{\circ} \approx \Sigma$$
 BE (broken bonds) – Σ BE (formed bonds)

We have to break 1 C-H bond and 1 Cl-Cl bond and form 1 C-Cl bond and 1 H-Cl bond

Thus,

$$\Delta_r H^\circ \approx \Sigma \text{ BE (broken bonds)} + \Sigma \text{ BE (formed bonds)} \stackrel{C=0}{\subset =0}$$

$$= (413 + 242) - (328 + 431)$$

$$= -104 \text{ kJ/mol}$$

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С—Н	413	N—H N—N	391		O-H	463	F-F	155
C-N	293	N-O	201		O-F	190	Cl—F	253
C-O C-F	358 485	N—F N—Cl	272 200		O—Cl	203 234	Cl—Cl	242
C-CI	328	N-Br	243		0 /11	220	Br—F	237
C I	2/6 240	н—н	436		S—H S—F	339 327	Br—Cl Br—Br	218 193
C—s	259	H-F	567		S—Cl	253	I (1	200
Si—H	323	H—Br	366)	S—Br S—S	266	I—CI I—Br	208175
Si—Si Si—C	226 301	H—I	299				I-I	151
	C-H C-C C-N C-O C-F C-Cl C-Br C-I C-S	C—H 413 C—C 348 C—N 293 C—O 358 C—F 485 C—C1 328 C—Br 276 C—I 240 C—S 259 Si—H 323 Si—Si 226	C—H 413 N—H C—C 348 N—N C—N 293 N—O C—O 358 N—F C—F 485 N—C1 C—C1 328 N—Br C—Br 276 C—I 240 H—H C—S 259 H—F H—C1 Si—H 323 H—Br Si—Si 226 H—I	C—H 413 N—H 391 C—C 348 N—N 163 C—N 293 N—O 201 C—O 358 N—F 272 C—F 485 N—C1 200 C—C1 328 N—Br 243 C—Br 276 C—I 240 H—H 436 C—S 259 H—F 567 H—C1 431 Si—H 323 H—Br 366 Si—Si 226 H—I 299	C—H 413 N—H 391 C—C 348 N—N 163 C—N 293 N—O 201 C—O 358 N—F 272 C—F 485 N—C1 200 C—C1 328 N—Br 243 C—Br 276 C—I 240 H—H 436 C—S 259 H—F 567 H—C1 431 Si—H 323 H—Br 366 Si—Si 226 H—I 299	C-H 413 N-H 391 O-H C-C 348 N-N 163 O-O C-N 293 N-O 201 O-F C-O 358 N-F 272 O-Cl C-F 485 N-Cl 200 O-I C-Cl 328 N-Br 243 C-Br 276 S-H C-I 240 H-H 436 S-F C-S 259 H-F 567 S-Cl H-Cl 431 S-Br Si-H S-S S-S Si-Si 226 H-I 299	C-H 413 N-H 391 O-H 463 C-C 348 N-N 163 O-O 146 C-N 293 N-O 201 O-F 190 C-O 358 N-F 272 O-Cl 203 C-F 485 N-Cl 200 O-I 234 C-Cl 328 N-Br 243 S-H 339 C-Br 276 S-H 339 S-F 327 C-S 259 H-H 436 S-F 327 C-S 259 H-F 567 S-Cl 253 H-Cl 431 S-Br 218 Si-H 323 H-Br 366 S-S 266 Si-Si 226 H-I 299 S-S 266	C-H 413 N-H 391 O-H 463 F-F C-C 348 N-N 163 O-O 146 C-N 293 N-O 201 O-F 190 Cl-F C-O 358 N-F 272 O-Cl 203 Cl-Cl C-F 485 N-Cl 200 O-I 234 Br-F C-Cl 328 N-Br 243 Br-F S-H 339 Br-Cl C-Br 276 S-H 339 Br-Cl Br-Br Br-Br C-I 240 H-H 436 S-F 327 Br-Br Br-Br C-S 259 H-F 567 S-Cl 253 I-Cl I-Br Si-H 323 H-Br 366 S-S 266 I-Br Si-Si 226 H-I 299 I-I I-I

Multiple Bonds C=C 614 N=N

$$C = C$$
 614
 $N = N$
 418
 O_2
 495

 $C = C$
 839
 $N = N$
 941

 $C = N$
 615
 $N = O$
 607
 $S = O$
 523

 $C = N$
 891
 $S = O$
 523
 53
 5418

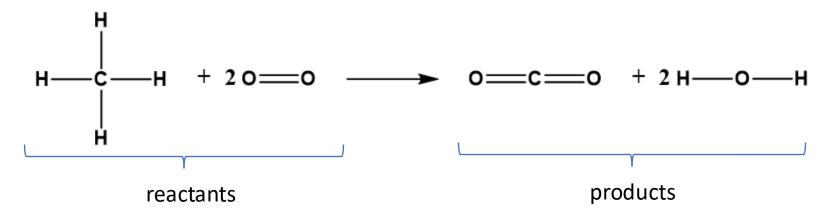
C = O 1072

so this will be an exothermic reaction.

Practice Problem: Use average bond enthalpy data to estimate the enthalpy change for the complete combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Step 1: Draw the molecular structures (show bonds) for the molecules involved in the reaction



Step 2: Determine the type and number of bonds that need to be <u>broken</u> for reactants and the type of number of bonds that need to be <u>formed</u> to give products.

4 C-H and 2 O=O bonds need to be broken 2 C=O and 4 O-H bonds will form

Step 3: Estimate ΔH for the reaction using the following equation:

$$\Delta_r H^\circ \approx \Sigma$$
 BE (broken bonds) – Σ BE (formed bonds)

$$= 2642 \text{ kJ/mol} - 3450 \text{ kJ/mol}$$

$$= -808 \text{ kJ/mol}$$

Average bond enthalpies (in kJ/mol)

Single E	Bonds						
С-Н	413	N-H	391	о-н	463	F-F	155
C-C	348	N-N	163	o-o	146		
C-N	293	N-O	201	O-F	190	Cl-F	253
C-O	358	N-F	272	O-Cl	203	Cl-Cl	242
C-F	485	N-C1	200	O-I	234		
C-Cl	328	N-Br	243			Br - F	237
C-Br	276			S-H	339	Br-Cl	218
C-I	240	H-H	436	S-F	327	Br - Br	193
C-S	259	H-F	567	S-CI	253		
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Si—Si	226	H-I	299			I-I	151
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C=C	614	N=N	418	O_2	495		
$C \equiv C$	839	$N \equiv N$	941	_			
C=N	615	N=0	607	s=0	523		
$C \equiv N$	891			s=s	418		
c=0	799						
$C \equiv O$	1072						
and the second	and any of the control						

Experimentally, ΔH_{comb} for CH₄ is known to be -890 kJ/mol.

Spontaneous and Non-Spontaneous Reactions

- Energy changes are important when thinking of the feasibility of a process or reaction
 - By knowing or being able to calculate the enthalpy change(s) involved we can determine the thermal energy that must be supplied or what we expect to obtain
- A **Spontaneous process** is a process that occurs in a system left to itself
 - once started, no action from outside is necessary to make the process continue.
- A Non-spontaneous process will not occur unless some external action is continuously applied
- Is the energy change associated with the process (i.e. enthalpy) the only consideration for establishing whether the process is **spontaneous** or **non-spontaneous**?

4 Fe + 3
$$O_2 \rightarrow 2 \text{ Fe}_2 O_3$$

$$\Delta_r H^\circ = -1648.4 \text{ kJ/mol}$$

Spontaneous

$$Ba(OH)_{2^{\bullet}} H_{2}O_{(s)} + NH_{4}CI_{(s)} \rightarrow BaCI_{2(s)} + 10 H_{2}O_{(I)} + 2NH_{3(g)}$$

$$\Delta_r H^\circ = + 165 \text{ kJ/mol}$$

Spontaneous As well!

Clearly enthalpy change for a process is <u>not</u> the only criterion for predicting direction of spontaneous change.
 To better predict spontaneity we will need to examine another system property, Entropy! (See <u>Ch. 16.2</u> later in course)