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

Learning Objective	Openstax 2e Chapter
Thermochemistry of Combustion	5.3
Bond Energy and Enthalpy	†
Introduction to Spontaneity	16.1

†See the complementary e-textbook:
- First Year General Chemistry by Mombourquette, Chapter 7.6

Suggested Practice Problems

Chapter 5 Exercises – Questions: 45*, 49, 51*, 57*, 73*, 79, 81

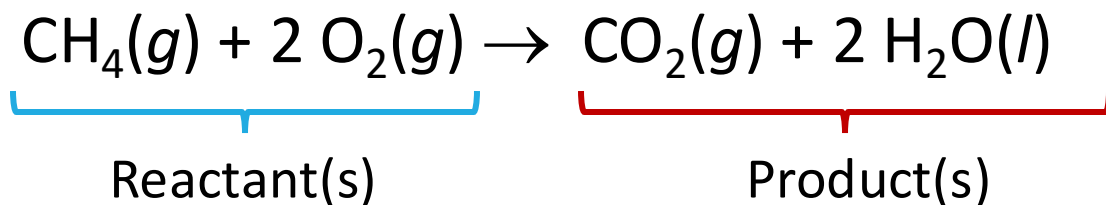Answers can be found in the Chapter 5 Answer Key

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

TABLE 7.4
Approximate Heats of Combustion of Some Fuels

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

Heat of Combustion

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

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

Reactant(s)   Product(s)

TABLE 7.2 Some Standard Molar Enthalpies of Formation, $\Delta_f H°$ at 298.15 K

Substance	kJ/mol[a]	Substance	kJ/mol[a]
CO(g)	−110.5	HBr(g)	−36.40
CO₂(g)	−393.5	HI(g)	26.48
CH₄(g)	−74.81	H₂O(g)	−241.8
C₂H₂(g)	226.7	H₂O(l)	−285.8
C₂H₄(g)	52.26	H₂S(g)	−20.63
C₂H₆(g)	−84.68	NH₃(g)	−46.11
C₃H₈(g)	−103.8	NO(g)	90.25
C₄H₁₀(g)	−125.6	N₂O(g)	82.05
CH₃OH(l)	−238.7	NO₂(g)	33.18
C₂H₅OH(l)	−277.7	N₂O₄(g)	9.16
HF(g)	−271.1	SO₂(g)	−296.8
HCl(g)	−92.31	SO₃(g)	−395.7

[a]Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Solution:

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

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

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

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 <u>estimate</u> $\Delta_r H^0$.**

Note that:

- **Average bond enthalpies are all positive!**

- These are <u>average</u> bond enthalpies; the C—H bonds in methane, CH_4, will be a bit different than the C—H bond in chloroform, $CHCl_3$.

- Bond forming reaction is exothermic

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

- Bond breaking reaction is endothermic

  $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta_r H^o$ = +242 kJ/mol
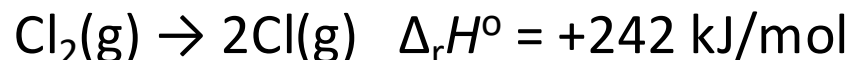
Table of average bond enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	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—Cl	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			S—F	327	Br—Br	193
C—S	259	H—H	436	S—Cl	253		
		H—F	567	S—Br	218	I—Cl	208
Si—H	323	H—Cl	431	S—S	266	I—Br	175
Si—Si	226	H—Br	366			I—I	151
Si—C	301	H—I	299				
Si—O	368						
Si—Cl	464						

Multiple Bonds

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=S	418
C=O	799				
C≡O	1072				

Now we can use average bond enthalpies to *estimate* enthalpy of reaction ($\Delta_r H°$)

Estimate $\Delta_r H°$ for the reaction:

$$CH_4 (g) + Cl_2 (g) \rightarrow CH_3Cl (g) + HCl (g)$$
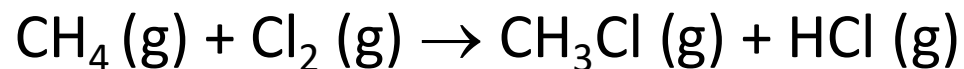
$\Delta_r H° \approx \Sigma$ BE (broken bonds) $- \Sigma$ BE (formed bonds)

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,

$\Delta_r H° \approx \Sigma$ BE (broken bonds) $+ \Sigma$ BE (formed bonds)

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

$= -104$ kJ/mol

so this will be an exothermic reaction.

average bond enthalpies (kJ/mol)

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

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
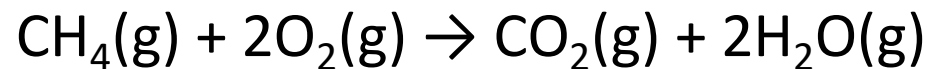
Step 1: Draw the molecular structures (show bonds) for the molecules involved in the reaction

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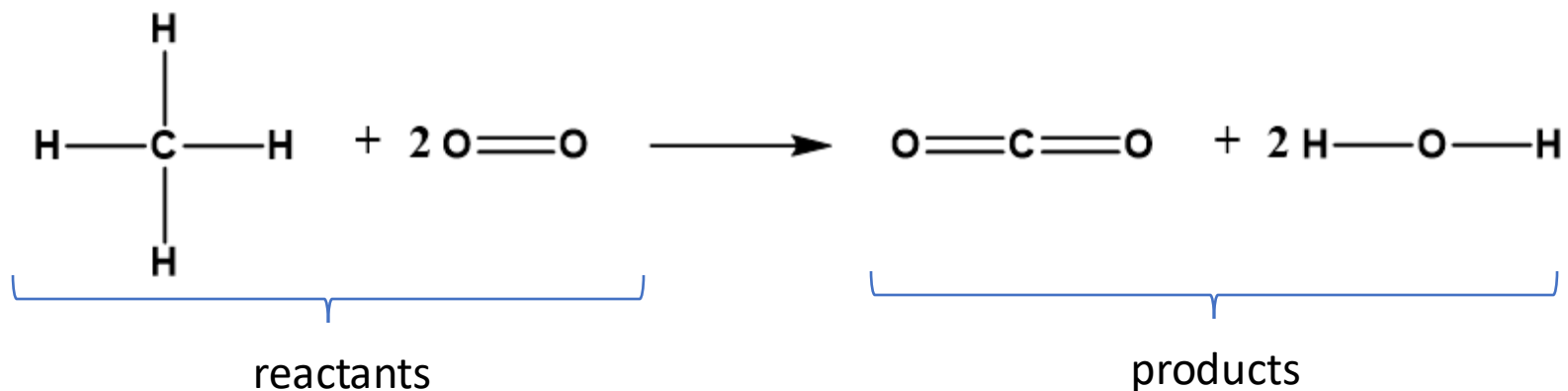
Step 2: Determine the type and number of bonds that need to be <u>broken</u> for reactants and the type of number of bonds that need to be <u>formed</u> to give products.

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:

$$\Delta_r H° \approx \Sigma \; BE \; \text{(broken bonds)} - \Sigma \; BE \; \text{(formed bonds)}$$

= [4 x (413 kJ/mol) + 2 x (495 kJ/mol)]

   4   C–H bonds   2 O=O bonds

– [2 x (799 kJ/mol) + 4 x (463 kJ/mol)]

   2 C=O bonds   4   O–H bonds

= 2642 kJ/mol – 3450 kJ/mol

= -808 kJ/mol

Experimentally, ΔH_{comb} for CH_4 is known to be -890 kJ/mol.

Average bond enthalpies (in kJ/mol)

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C—H	413	N—H	391	O—H	463	F—F	155
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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?**
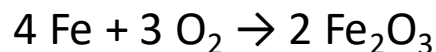
$$4 \text{ Fe} + 3 \text{ O}_2 \rightarrow 2 \text{ Fe}_2\text{O}_3 \qquad\qquad \Delta_r H° = -1648.4 \text{ kJ/mol} \qquad \textbf{Spontaneous}$$

$$\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}_{(s)} + \text{NH}_4\text{Cl}_{(s)} \rightarrow \text{BaCl}_{2(s)} + 10 \text{ H}_2\text{O}_{(l)} + 2\text{NH}_{3(g)} \qquad \Delta_r H° = +165 \text{ kJ/mol} \qquad \textbf{Spontaneous As well!}$$

- 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 Ch. 16.2 later in course)