# Bond Energies

5.3

Ethyne, $C_2H_2$, is a colourless hydrocarbon commonly known as acetylene. This compound burns readily to produce flames with temperatures greater than 3000 °C. At these temperatures, a torch burning a mixture of oxygen and acetylene can cut through steel (**Figure 1**). Oxyacetylene torches are also used for welding metals together. However, many welders today use electric welding torches.

Is it possible to predict how much energy the combustion of acetylene releases? The answer is yes; you can estimate the enthalpy change of any chemical reaction if you know the quantity of energy associated with the chemical bonds of both the reactants and products.

**Figure 1** A worker in heat-resistant protective clothing uses an oxyacetylene torch to cut steel.

## Measuring Bond Energies

A covalent bond between 2 atoms will break if enough energy is supplied. The quantity of energy required to break a chemical bond is its **bond dissociation energy**. Bond dissociation energies have positive values. For example, a single covalent C–H bond in a hydrocarbon (such as methane or propane) has an average bond energy of 413 kJ/mol. This means that it takes 413 kJ of energy to break 1 mol of C–H bonds into 1 mol of C atoms and 1 mol of H atoms. Conversely, when a C–H bond forms, 413 kJ of energy is released, in keeping with the law of conservation of energy. **Table 1** lists average bond energies for several covalent bonds.

**bond dissociation energy** the energy required to break a given chemical bond

**Table 1** Average Bond Energies (kJ/mol)

| Single bonds | | | Multiple bonds |
|---|---|---|---|
| H–H 432 | N–H 391 | I–I 149 | C=C 614 |
| H–F 565 | N–N 160 | I–Cl 208 | C≡C 839 |
| H–Cl 427 | N–F 272 | I–Br 175 | O=O 495 |
| H–Br 363 | N–Cl 200 | S–H 347 | C=O* 745 |
| H–I 295 | N–Br 243 | S–F 327 | C≡O 1072 |
| C–H 413 | N–O 201 | S–Cl 253 | N=O 607 |
| C–C 347 | O–H 467 | S–Br 218 | N=N 418 |
| C–N 305 | O–O 146 | S–S 266 | N≡N 941 |
| C–O 358 | O–F 190 | Si–Si 340 | C≡N 891 |
| C–F 485 | O–Cl 203 | Si–H 393 | C=N 615 |
| C–Cl 339 | O–I 234 | Si–C 360 | |
| C–Br 276 | F–F 154 | Si–O 452 | |
| C–I 240 | F–Cl 253 | | |
| C–S 259 | F–Br 237 | | |
| | Cl–Cl 239 | | |
| | Cl–Br 218 | | |
| | Br–Br 193 | | |

*C=O in $CO_2(g)$=799

Why are bond dissociation energies reported as average bond energies? The bond dissociation energy of a given bond depends on the types of atoms and bonds in the same molecule.

For example, consider the stepwise decomposition of methane and the energy required for each step to occur:

| Process | Energy Required (kJ/mol) |
| --- | --- |
| $CH_4(g) \rightarrow CH_3(g) + H(g)$ | 435 |
| $CH_3(g) \rightarrow CH_2(g) + H(g)$ | 453 |
| $CH_2(g) \rightarrow CH(g) + H(g)$ | 425 |
| $CH(g) \rightarrow C(g) + H(g)$ | 339 |
| | Total = 1652 |

$$\text{Average} = \frac{1652}{4} = 413$$

Although a C–H bond is broken in each step, a different amount of energy is required each time. This shows that the bond energy of a C–H bond is affected by the number of atoms and bonds around it. Therefore, 413 kJ/mol only approximates the energy associated with a C–H bond in a particular molecule. The use of an average bond energy is convenient for predicting enthalpy changes in chemical reactions.

## Multiple Bonds and Bond Energies

Notice in the data given in Table 1 (page 307) that multiple bonds have larger bond energies than single bonds. For example, 839 kJ/mol of energy is required to break a triple bond between carbon atoms. Breaking a double bond between carbon atoms requires only 614 kJ/mol of energy, and it takes only 347 kJ/mol of energy to break a single C–C bond. This suggests that multiple bonds are generally stronger than single bonds.

A relationship also exists between the number of bonds between atoms (that is, number of electrons shared) and the length of a covalent bond (that is, distance between nuclei): as the number of bonds increases, the bond length shortens (**Table 2**).

**Table 2** Bond Lengths of Some Common Bonds

| Bond | Bond type | Bond length (pm) | Bond energy (kJ/mol) |
| --- | --- | --- | --- |
| C–C | single | 154 | 347 |
| C=C | double | 134 | 614 |
| C≡C | triple | 120 | 839 |
| C–O | single | 143 | 358 |
| C=O | double | 123 | 745 |
| C–N | single | 143 | 305 |
| C=N | double | 138 | 615 |
| C≡N | triple | 116 | 891 |

## Enthalpy and Bond Energies

Bond energy values can be used to calculate approximate enthalpy changes, $\Delta H$, for reactions. During a chemical reaction, the bonds in the reactants must first break. For bonds to be broken, energy must be *added*—an endothermic process. Hence, energy terms associated with bond breaking have *positive* signs. Making new bonds in the products *releases* energy—an exothermic process. Therefore, energy terms associated with bond making have *negative* signs.

We can write the enthalpy change for a reaction as

$$\Delta H = \begin{array}{l}\text{sum of energies required}\\\text{to break old bonds}\\\text{(positive values)}\end{array} + \begin{array}{l}\text{sum of energies released in}\\\text{the formation of new bonds}\\\text{(negative values)}\end{array}$$

This leads to the equation

$$\Delta H = \underbrace{\Sigma n \times D\ \text{(bonds broken)}}_{\text{energy required}} - \underbrace{\Sigma n \times D\ \text{(bonds formed)}}_{\text{energy released}}$$

where the symbol Σ (sigma) means "the sum of," $n$ is the amount (in moles) of a particular bond type, and $D$ is the bond energy per mole of bonds. $D$ is always a positive value. The value of $D$ is obtained from reference tables, such as Table 1 (page 307).

The first step in using bond energies to predict $\Delta H$ for a reaction is to determine how many of each type of bond must be broken in the reactants. Next, determine the number of bonds of each type that form in the products. Finally, use bond energy data from Table 1 (page 307) to calculate the total energy required to break the reactant bonds, followed by the total energy released by the formation of product bonds. The energy change, $\Delta H$, of the reaction is the difference between these two sums.

## Tutorial 1 Estimating Enthalpy Change from Bond Energies

In this tutorial, you will use bond energies to calculate an approximate value of the enthalpy change, $\Delta H$, for a number of different chemical reactions. (Note that in this tutorial Table 1 on page 307 is referenced often.)

### Sample Problem 1: Using Bond Energies and a Balanced Chemical Equation to Estimate $\Delta H$

Using the bond energies in Table 1, calculate the enthalpy change for the reaction in which hydrogen gas, $H_2(g)$, is combined with fluorine gas, $F_2(g)$, to produce 2 moles of hydrogen fluoride gas, HF(g). This reaction is represented by the balanced chemical equation:

$$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$$

**Given:** for $H_2(g)$: $n_{H-H} = 1$ mol; $D_{H-H} = 432$ kJ/mol;
for $F_2(g)$: $n_{F-F} = 1$ mol; $D_{F-F} = 154$ kJ/mol;
for HF(g): $n_{H-F} = 2$ mol; $D_{H-F} = 565$ kJ/mol

**Required:** $\Delta H$

**Analysis:** $\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$

$$\Delta H = (n_{H-F}D_{H-F} + n_{F-F}D_{F-F}) - n_{H-F}D_{H-F}$$

**Solution:**

1 mol each of H–H and F–F bonds are broken. The bonds formed are 2 mol of H–F bonds. Therefore,

$$\Delta H = (n_{H-F}D_{H-F} + n_{F-F}D_{F-F}) - n_{H-F}D_{H-F}$$

$$= (1\ \text{mol} \times D_{H-H} + 1\ \text{mol} \times D_{F-F}) - 2\ \text{mol} \times D_{H-F}$$

$$= \left[\left(1\ \cancel{\text{mol}} \times \frac{432\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(1\ \cancel{\text{mol}} \times \frac{154\ \text{kJ}}{\cancel{\text{mol}}}\right)\right] - \left(2\ \cancel{\text{mol}} \times \frac{565\ \text{kJ}}{\cancel{\text{mol}}}\right)$$

$$\Delta H = -544\ \text{kJ}$$

**Statement:** The reaction of 1 mol of hydrogen gas and 1 mol of fluorine gas to produce 2 mol of hydrogen fluoride releases 544 kJ of energy. Thus, the enthalpy change ($\Delta H$) is −544 kJ.

### Sample Problem 2: Using Bond Energies and Lewis Diagrams to Estimate $\Delta H$

Using the bond energies in Table 1, calculate the enthalpy change for the reaction in which methane gas, $CH_4(g)$, is combined with chlorine gas and fluorine gas to produce

Freon-12 gas, $CF_2Cl_2(g)$. **Figure 2** shows the Lewis structures of methane and Freon-12. The balanced chemical equation for the formation of 1 mol of Freon-12 is

$$CH_4(g) + 2\,Cl_2(g) + 2\,F_2(g) \rightarrow CF_2Cl_2(g) + 2\,HF(g) + 2\,HCl(g)$$

methane Freon-12

**Figure 2**

## Solution

**Step 1.** For each reactant and product, identify the number of moles of bonds, the amount of bonds in the reaction, and the bond energy per mole (using the data in Table 1). Organize this information in a table, similar to **Table 3.**

**Table 3** Bonds and Bond Energies in Reactants and Products

| | Substance | Number of bonds moles of ($n_{substance}$) | Amount of bonds in reaction | Bond energy per mole |
|---|---|---|---|---|
| reactants | $CH_4(g)$ | 4 mol C–H bonds | 4 mol | 413 kJ/mol |
| | $Cl_2(g)$ | 1 mol Cl–Cl bonds | 2 mol | 239 kJ/mol |
| | $F_2(g)$ | 1 mol F–F bonds | 2 mol | 154 kJ/mol |
| products | $CF_2Cl_2(g)$ | 2 mol C–F bonds<br>2 mol C–Cl bonds | 2 mol<br>2 mol | 485 kJ/mol<br>339 kJ/mol |
| | HF(g) | 1 mol H–F bonds | 2 mol | 565 kJ/mol |
| | HCl(g) | 1 mol H–Cl bonds | 2 mol | 427 kJ/mol |

**Step 2.** Calculate the enthalpy change, $\Delta H$, of the reaction.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$

$$\Delta H = (nD_{C-H} + nD_{Cl-Cl} + nD_{F-F}) - (nD_{C-F} + nD_{C-Cl} + nD_{H-F} + nD_{H-Cl})$$

For convenience, first add the total energy absorbed to break the bonds in the reactants:

$$\begin{aligned}
\Sigma n \times D_{\text{bonds broken}} &= (nD_{C-H} + nD_{Cl-Cl} + nD_{F-F}) \\
&= \left(4\ \cancel{\text{mol}} \times \frac{413\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{239\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{154\ \text{kJ}}{\cancel{\text{mol}}}\right) \\
&= 1652\ \text{kJ} + 478\ \text{kJ} + 308\ \text{kJ} \\
\Sigma n \times D_{\text{bonds broken}} &= 2438\ \text{kJ}
\end{aligned}$$

This is the energy required to break the bonds in the reactants.

Now, add the total energy released when the bonds of products form.

$$\begin{aligned}
\Sigma n \times D_{\text{bonds formed}} &= (nD_{C-F} + nD_{C-Cl} + nD_{H-F} + nD_{H-Cl}) \\
&= \left(2\ \cancel{\text{mol}} \times \frac{485\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{339\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{565\ \text{kJ}}{\cancel{\text{mol}}}\right) + \\
&\qquad \left(2\ \cancel{\text{mol}} \times \frac{427\ \text{kJ}}{\cancel{\text{mol}}}\right) \\
&= 970\ \text{kJ} + 678\ \text{kJ} + 1130\ \text{kJ} + 854\ \text{kJ} \\
\Sigma n \times D_{\text{bonds formed}} &= 3632\ \text{kJ}
\end{aligned}$$

This is the energy released when the bonds are formed in the products.

Subtract the energy released when the bonds of the products form from the energy absorbed to break the bonds of the reactants.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$
$$= 2438 \text{ kJ} - 3632 \text{ kJ}$$
$$\Delta H = -1194 \text{ kJ}$$

The sign of the enthalpy change in the formation Freon-12 gas is negative. This is an exothermic reaction and energy is released.

**Statement:** When 1 mol of Freon-12 gas is formed by reacting gaseous methane, chlorine, and fluorine, 1194 kJ of energy is released. Thus, the enthalpy change ($\Delta$H) is $-1194$ kJ.

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### **Sample Problem 3:** Using Bond Energies and Chemical Structures to Estimate $\Delta H$

Using bond energies from Table 1, determine whether the complete combustion of ethyne gas (acetylene), $C_2H_2(g)$, to carbon dioxide gas and liquid water is exothermic or endothermic.

### Solution

**Step 1.** Write the balanced chemical equation for the combustion of 1 mol of ethyne:

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$$

**Step 2.** Determine the bonding of each substance by drawing structural formulas for each molecule in the reaction:

$H-C\equiv C-H$

$C_2H_2(g)$

$O=O$

$O_2(g)$

$O=C=O$

$CO_2(g)$

$$\begin{array}{l} O-H \\ | \\ H \end{array}$$

$H_2O(g)$

**Step 3.** Determine the number of moles of reactants and products, the number of moles of bonds broken or formed, and the molar bond energy for each. Organize this information in a table, similar to **Table 4.**

**Table 4** Bonds and Bond Energies in Reactants and Products

| | Substance | Number of moles of bonds ($n_{\text{substance}}$) | Amount of bonds in reaction | Bond energy per mole |
|---|---|---|---|---|
| reactants | $C_2H_2(g)$ | 2 mol C–H bonds<br>1 mol C≡C bonds | 2 mol<br>1 mol | 413 kJ/mol<br>839 kJ/mol |
| | $O_2(g)$ | 1 mol O=O bonds | $\frac{5}{2}$ mol | 495 kJ/mol |
| products | $CO_2(g)$ | 2 mol C=O bonds | 4 mol | 799 kJ/mol |
| | $H_2O(g)$ | 2 mol H–O bonds | 2 mol | 467 kJ/mol |

Note that in Table 1, the asterisk indicates that $CO_2(g)$ has a different $\Delta H$ than a regular C=O double bond.

**Step 4.** Calculate the enthalpy change, $\Delta H$, of the reaction.

$$\Delta H = \Sigma n \times D_{\text{bonds broken}} - \Sigma n \times D_{\text{bonds formed}}$$

$$\Delta H = (n_{\text{C-H}}D_{\text{C-H}} + n_{\text{C}\equiv\text{C}}D_{\text{C}\equiv\text{C}} + n_{\text{O=O}}D_{\text{O=O}}) - (n_{\text{C=O}}D_{\text{C=O}} + n_{\text{H-O}}D_{\text{H-O}})$$

$$= \left[\left(2\ \cancel{\text{mol}} \times \frac{413\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(1\ \cancel{\text{mol}} \times \frac{839\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(\frac{5}{2}\ \cancel{\text{mol}} \times \frac{495\ \text{kJ}}{\cancel{\text{mol}}}\right)\right] - \left[\left(4\ \cancel{\text{mol}} \times \frac{799\ \text{kJ}}{\cancel{\text{mol}}}\right) + \left(2\ \cancel{\text{mol}} \times \frac{467\ \text{kJ}}{\cancel{\text{mol}}}\right)\right]$$

$$= (826\ \text{kJ} + 839\ \text{kJ} + 1237.5\ \text{kJ}) - (3196\ \text{kJ} + 934\ \text{kJ})$$

$$= 2902.5\ \text{kJ} - 4130\ \text{kJ}$$

$$\Delta H = -1228\ \text{kJ}$$

**Statement:** When enthalpy change has a negative value, there is more energy released by the formation of the bonds in the products than is absorbed by the breaking of the bonds in the reactants. Therefore, thermal energy is released to the surroundings, and the reaction is exothermic.

## Practice

1. Use the data from Table 1 to calculate the energy to separate 1 mol of chloromethane, $CH_3Cl(g)$, into free atoms. K/U T/I [ans: 1578 kJ/mol]
2. Using bond energies, verify that the complete combustion of ethene gas, $C_2H_4(g)$ ($H_2C{=}CH_2$), to gaseous carbon dioxide and water is an exothermic reaction. K/U T/I [ans: −1313 kJ]
3. Using the data from Table 1, calculate the enthalpy change of the chemical reaction represented by the balanced equation

   $N_2H_2(g) + F_2(g) \rightarrow N_2(g) + 2\ HF(g)$

   Is the reaction endothermic or exothermic? Explain. K/U T/I [ans: −717 kJ; exothermic]
4. Propane, $C_3H_8(g)$, is a gaseous fuel that burns with oxygen. Write the balanced chemical equation for this complete combustion reaction, and use the bond energies from Table 1 to calculate the quantity of energy released. K/U T/I A [ans: −2057 kJ ]

The bonds between specific atoms and the bond energies associated with these bonds are very similar, even when the bonds are located in different entities. For example, the bond energy of the C–H bond in methane is similar to the bond energies of the C–H bonds in ethane, $C_2H_6(g)$; ethyne, $C_2H_2$ (g); and chloromethane, $CH_3Cl$ (g). Thus, molecules with similar bonds act in similar ways.

Since the bond energies of similar bonds are nearly the same in different molecules, you can calculate and compare the enthalpy changes of reactions by using bond energies because they provide a good approximation of the actual bond energy value. For example, in Sample Problem 3 in Tutorial 1, you calculated an enthalpy change of −1227 kJ/mol for the combustion reaction of acetylene gas. The experimental value of this reaction is −1299 kJ/mol. CAREER LINK

# 5.3 Review

## Summary

- Bond energy is the quantity of energy required to break a chemical bond.
- As the number of bonds increases, the bond length shortens.
- More energy is needed to break multiple bonds than to break single bonds.
- Bond breaking is an endothermic process.
- Bond making is an exothermic process.
- An approximate value of the $\Delta H$ of a reaction can be calculated using the bond energies of the reactants and products.

## Questions

1. Use bond energy values (Table 1, page 307) to estimate $\Delta H$ for the reactions represented by the following equations: K/U T/I
   (a) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$
   (b) $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$
2. Use bond energy values (Table 1, page 307) to estimate $\Delta H$ for the reactions represented by the following equations: K/U T/I
   (a) $HCN(g) + 2\,H_2(g) \rightarrow CH_3NH_2(g)$
   (b) $N_2H_4(g) + 2\,F_2(g) \rightarrow N_2(g) + 4\,HF(g)$
3. Explain why $\Delta H$ values of chemical reactions are found using bond energies that are not always equal to values found by experiment. Assume experimental error is not a factor. K/U T/I
4. Consider the reaction represented by the equation

   $A_2 + B_2 \rightarrow 2\,AB \quad \Delta H = -549\text{ kJ}$

   The bond energy for $A_2$ is one-half the AB bond energy. The bond energy of $B_2$ is 432 kJ/mol. Calculate the bond energy of $A_2$. K/U T/I
5. In which molecule, $N_2$, $N_2H_2$ or $N_2O_4$, would the nitrogen–nitrogen bond be the shortest, and why? Draw Lewis structures to help you decide. K/U T/I C
6. Explain why the numerical value of a carbon–carbon bond in a molecule of ethanol would differ from that in a molecule of ethane. Include Lewis structures for ethanol and ethane in your explanation. K/U T/I C
7. The bond energy of a C–O single bond is less than the bond energy of a C=O double bond. Explain why this is true. K/U T/I
8. Acetic acid is responsible for the sour taste of vinegar. Acetic acid can be manufactured using the reaction represented by the equation

   $CH_3OH(g) + CO(g) \rightarrow CH_3COOH(l)$

   Use bond energy values from Table 1 (page 307) to estimate the $\Delta H$ for this reaction. K/U T/I
9. Consider the reaction represented by the equation

   $C_2H_4(g) + F_2(g) \rightarrow C_2H_4F_2(g) \quad \Delta H = -549\text{ kJ}$

   Estimate the carbon–fluorine bond energy, given that the C–C bond energy is 347 kJ/mol, the C=C bond energy is 614 kJ/mol, and the F–F bond energy is 154 kJ/mol. K/U T/I
10. In photosynthesis, a plant converts carbon dioxide and water to glucose, $C_6H_{12}O_6(s)$, and oxygen. Use bond energy values from Table 1 (page 307) to estimate the amount of energy the Sun provides to produce 1 mol of glucose. Assume the straight-chain version of glucose (p. 101). K/U T/I
11. Carbon monoxide, $CO(g)$, can react with oxygen, $O_2(g)$, to produce carbon dioxide, $CO_2(g)$. Use bond energy values from Table 1 (page 307) to determine if this reaction is exothermic or endothermic. K/U T/I
12. Carbon dioxide, $CO_2(g)$, can react with water, $H_2O(l)$, to produce carbonic acid, $H_2CO_3(aq)$, a component of acid rain. K/U T/I C
    (a) Write a balanced equation for this reaction.
    (b) Use Lewis structures to illustrate this reaction.
    (c) Determine the energy required to convert 1 mol of carbon dioxide to 1 mol of carbonic acid.
13. Many barbecues are fuelled by propane, $C_3H_8(g)$. Other barbecues are fuelled by natural gas, which is mostly methane, $CH_4(g)$. K/U T/I
    (a) Use bond energy values to estimate the amount of heat produced by the complete combustion of 1 mol of propane, and of 1 mol of methane.
    (b) How many moles of natural gas are needed to produce the same amount of energy as 1.0 mol of propane?