Pearson

9.9: Determining Enthalpies of Reaction from Bond Energies

In Section 9.7, we saw that we can *measure* ΔH for a chemical reaction with calorimetry. In this section we turn to *estimating* ΔH for a chemical reaction from bond energies.

We saw in Section 9.6 that the energy changes associated with chemical reactions correspond to potential energy changes in the particles that compose atoms and molecules. In other words, during a chemical reaction, the *structure* of the particles that compose matter changes. That structure change causes a potential energy change that results in an energy exchange with the surroundings.

We can estimate the magnitude and sign of the energy exchange associated with a particular chemical reaction by focusing on the bonds that are broken and formed during the reaction. Recall from Section 5.6 that, based on experimental measurements, we can assign energies to specific bonds within a molecule (Table 9.3). These bond energies correspond to the amount of energy *necessary to break* the particular chemical bond, but they also correspond to the amount of energy *emitted* when the bond is formed. Therefore, by adding the energies associated with the bonds that break in a reaction (remember that endothermic processes such as bond breaking carry a positive sign), and subtracting the energies associated with the bonds that form (remember that exothermic processes such as bond formation carry a negative sign), we can estimate the overall ΔH for a reaction.

Table 9.3 Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N═N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N═O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C═C	611	O═O	498	Si═O	368
C≡C	837	O—F	190	S═O	523
C—N	305	O—Cl	203	Si—Cl	464
C═N	615	O—I	234	S═S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C═O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266

C=O	1072			S—S	266
C—Cl	339				

*799 in CO_2

For example, consider the reaction between methane and chlorine:

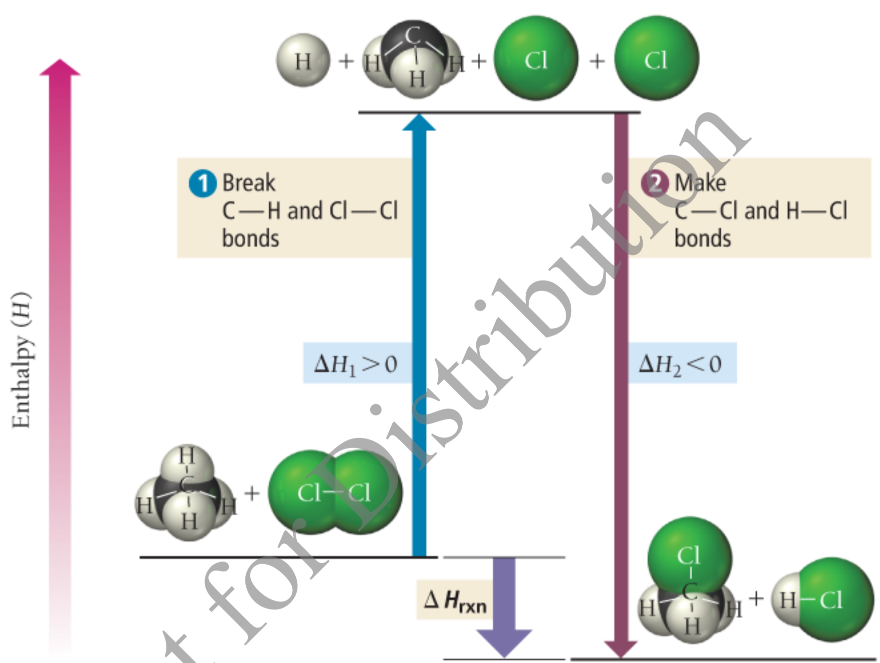
$$H_3C—H\,(g) + Cl—Cl\,(g) \rightarrow H_3C—Cl\,(g) + H—Cl\,(g)$$

We can imagine this reaction occurring by the breaking of a C–H bond and a Cl–Cl bond and the forming of a C–Cl bond and a H–Cl bond. So we can calculate the overall enthalpy change as a sum of the enthalpy changes associated with breaking the required bonds in the reactants and forming the required bonds in the products, as shown in Figure 9.10.

Figure 9.10 Estimating ΔH_{rxn} from Bond Energies

We can approximate the enthalpy change of a reaction by summing the enthalpy changes involved in breaking old bonds and forming new ones.

Estimating the Enthalpy Change of a Reaction from Bond Energies



$$H_3C—H(g) + Cl—Cl(g) \longrightarrow H_3C—Cl(g) + H—Cl(g)$$

Bonds Broken		Bonds Formed	
C—H break	+414 kJ	C—Cl form	−339 kJ
Cl—Cl break	+243 kJ	H—Cl form	−431 kJ
Sum (Σ)ΔHs bonds broken: +657 kJ		*Sum (Σ)ΔHs bonds formed:* −770 kJ	

$$\Delta H_{rxn} = \Sigma(\Delta H\text{s bonds broken}) + \Sigma(\Delta H\text{s bonds formed})$$
$$= +657\text{ kJ} - 770\text{ kJ} = -113\text{ kJ}$$

Using this method, we determine that $\Delta H_{rxn} = -113$ kJ. The actual $\Delta H^{\circ}_{rxn} = -101$ kJ, which is fairly close to the value we obtained from average bond energies. Bond energies don't give exact values for the change in enthalpy of a reaction because bond energies are average values obtained from measurements on many different molecules. Nonetheless, we can estimate ΔH_{rxn} from average bond energies fairly accurately by summing the ΔH values for the bonds broken and bonds formed. Remember that ΔH is positive for breaking bonds and negative for forming bonds.

$$\Delta H_{\text{rxn}} = \sum \underbrace{(\Delta H\text{s bonds broken})}_{\text{Positive}} + \sum \underbrace{(\Delta H\text{s bonds formed})}_{\text{Negative}}$$

As we can see from the above equation:

- A reaction is *exothermic* when weak bonds break and strong bonds form.
- A reaction is *endothermic* when strong bonds break and weak bonds form.

Scientists sometimes say that "energy is stored in chemical bonds or in a chemical compound," which may make it sound as if breaking the bonds in the compound releases energy. For example, in biology we often hear that energy is stored in glucose or in ATP. However, *breaking a chemical bond always requires energy*. When we say that energy is stored in a compound or that a compound is energy rich, we mean that the compound can undergo a reaction in which weak bonds break and strong bonds form, thereby releasing energy in the overall process. *Bond formation always releases energy*.

Conceptual Connection 9.8 **Bond Energies and ΔH_{rxn}**

Example 9.10 Calculating ΔH_{rxn} from Bond Energies

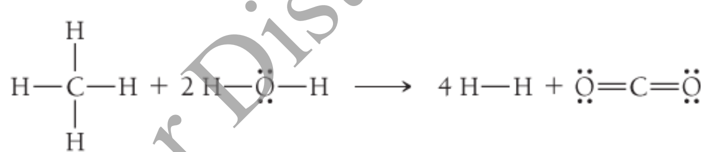
Hydrogen gas, a potential fuel, can be made by the reaction of methane gas and steam:

$$CH_4\,(g) + 2\,H_2O\,(g) \rightarrow 4\,H_2\,(g) + CO_2\,(g)$$

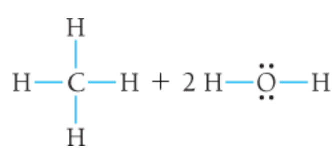
Use bond energies to calculate ΔH_{rxn} for this reaction.

SOLUTION

Begin by rewriting the reaction using the Lewis structures of the molecules involved.

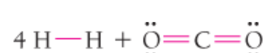


Determine which bonds are broken in the reaction and sum the bond energies of these. (Find bond energies in Table 9.3.)



$$\begin{aligned}&\Sigma\,(\Delta H\text{s bonds broken})\\ &= 4(\text{C—H}) + 4\,(\text{O—H}) = 4\,(414\text{ kJ}) + 4\,(464\text{ kJ}) = 3512\text{ kJ}\end{aligned}$$

Determine which bonds are formed in the reaction and sum the negatives of their bond energies.



$$\begin{aligned}&\Sigma\,(\Delta H\text{s bonds formed})\\ &= -4(\text{H—H}) - 2\,(\text{C}=\text{O}) = -4\,(436\text{ kJ}) - 2\,(799\text{ kJ}) = -3342\text{ kJ}\end{aligned}$$

Find ΔH_{rxn} by summing the results of the previous two steps.

$$\begin{aligned}\Delta H_{\text{rxn}} &= \Sigma(\Delta H\text{s bonds broken}) + \Sigma(\Delta H\text{s bonds fromed}) \\ &= 3512 - 3342 = 1.70 \times 10^2 \text{ kJ}\end{aligned}$$

FOR PRACTICE 9.10 Another potential future fuel is methanol (CH_3OH). Write a balanced equation for the combustion of gaseous methanol and use bond energies to calculate the enthalpy of combustion of methanol in kJ/mol.

FOR MORE PRACTICE 9.10 Use bond energies to calculate ΔH_{rxn} for this reaction:
$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$.

Interactive Worked Example 9.10 **Calculating ΔH_{rxn} from Bond Energies**