10.9: Determining Enthalpies of Reaction from Bond Energies

The heat changes which accompany a chemical reaction are caused largely by changes in the electronic energy of the molecules. If we restrict our attention to gases, and hence to fairly simple molecules, we can go quite a long way toward predicting whether a reaction will be exothermic by considering the bonds which are broken and made in the course of the reaction. In order to do this we must first become familiar with the idea of a bond enthalpy.

In other sections we point out that when a chemical bond forms, negative charges move closer to positive charges than before, and so there is a lowering of the energy of the molecule relative to the atoms from which it was made. This means that energy is required to break a molecule into its constituent atoms. The **bond enthalpy** D_{X-Y} of a diatomic molecule X—Y is the enthalpy change for the (usually hypothetical) process:

$$\mathrm{XY(g) \rightarrow X(g) + Y(g)}$$

$$\Delta H^o(298K) = D_{x-y}$$

We have already used the term **bond energy** to describe this quantity, though strictly speaking the bond energy is a measure of ΔU rather than ΔH. As we have already seen, ΔU and ΔH are nearly equal, and so either term may be used.

As an example, let us consider the bond enthalpy for carbon monoxide. It is possible to establish the thermochemical equation

$$\mathrm{CO(g) \rightarrow C(g) + O(g)}$$

$$\Delta H^o(298K) = 1073 kJ mol^{-1} \tag{10.9.1}$$

Accordingly we can write

$$\mathrm{C_{C\equiv O}{=}1073\,kJmol^{-1}}$$

even though the process to which Eq. 10.9.1 corresponds is hypothetical: Neither carbon nor oxygen exists as a monatomic gas at 298 K. For triatomic and polyatomic molecules, the bond enthalpy is usually defined as a mean. In the case of water, for instance, we have

$$\mathrm{H_2O(g) \rightarrow 2\,H(g) + O(g)}$$

$$\Delta H^o(298K) = 927.2\mathrm{kJ\ mol^{-1}}$$

Since it requires 927.2 kJ to break open *two* O—H bonds, we take *half* this value as the mean bond enthalpy and write

$$D_{O-H} = 463.6\mathrm{kJ\ mol^{-1}}$$

In methanol, CH_3OH,however, a value of 427 kJ mol^{-1} for the O—H bond enthalpy fits the experimental data better. In other words the strength of the O—H varies somewhat from compound to compound. Because of this fact, we must expect to obtain only approximate results, accurate only to about ± 50 kJ mol^{-1}, from the use of bond enthalpies. Bond enthalpies for both single and multiple bonds are given in Table 10.9.1.

TABLE 10.9.1 Average Bond Energies/kJ mol^{-1}.

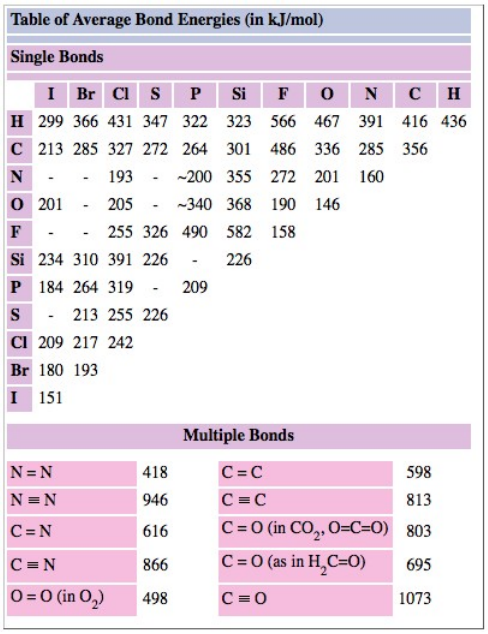


Table of Average Bond Energies (in kJ/mol)

Single Bonds

	I	**Br**	**Cl**	**S**	**P**	**Si**	**F**	**O**	**N**	**C**	**H**
H	299	366	431	347	322	323	566	467	391	416	436
C	213	285	327	272	264	301	486	336	285	356	
N	-	-	193	-	~200	355	272	201	160		
O	201	-	205	-	~340	368	190	146			
F	-	-	255	326	490	582	158				
Si	234	310	391	226	-	226					
P	184	264	319	-	209						
S	-	213	255	226							
Cl	209	217	242								
Br	180	193									
I	151										

Multiple Bonds

N = N	418	C = C	598
N ≡ N	946	C ≡ C	813
C = N	616	C = O (in CO_2, O=C=O)	803
C ≡ N	866	C = O (as in H_2C=O)	695
O = O (in O_2)	498	C ≡ O	1073

As an example of how a table of bond enthalpies can he used to predict the ΔH value for a reaction, let us take the simple case

$$\mathrm{H_2(g) + F_2(g) \rightarrow 2\,HF(g)} \tag{10.9.2}$$

298 K, 1 atm
We can regard this reaction as occurring in two stages (Figure 10.9.1). In the first stage all the reactant molecules are broken up into atoms:

$$\mathrm{H_2(g) + F_2(g) \rightarrow 2\,H(g) + F(g)} \tag{10.9.3}$$

298 K, 1 atm

For this stage

$$\Delta H_I = H_{H-H} + D_{F-F} \tag{10.9.4}$$

since 1 mol H_2 and 1 mol F_2 have been dissociated.

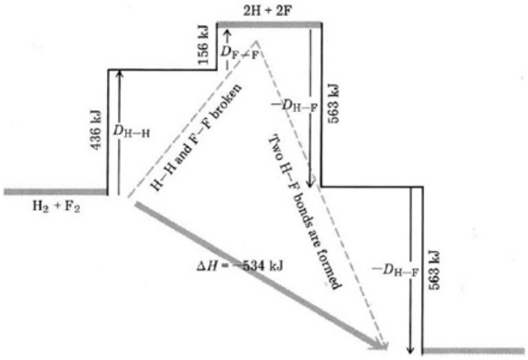


Figure 10.9.1 Bond-breaking-bond-making diagram for the reaction H_2 + F_2 + 2HF. When H_2 reacts with F_2, a strong H—H bond and a weak F—F bond are broken, while two extra-strong H—F bonds are made. The reaction is exothermic since more energy is released by the formation of the H—F bonds than is required to break the H—H and H—F bonds.

In the second stage the H and F atoms are reconstituted to form HF molecules:

$$\mathrm{2\,H(g) + 2\,F(g) \rightarrow 2\,HF(g)}$$

298 K, 1 atm

For which

$$\Delta H_{II} = -2D_{H-F}$$

where a negative sign is necessary since this stage corresponds to the *reverse* of dissociation.

Since Eq. 10.9.2 corresponds to the sum of Equations 10.9.3 and 10.9.4, Hess's law allows us to add ΔH values:

$$\Delta H^o_{reaction} = \Delta H_I + \Delta H_{II}$$

$$= D_{H-H} + D_{F-F} - 2DH - F$$

$$= (436 + 159 - 2 * 566)\text{kJ mol}^{-1}$$

$$= -539\text{kJ mol}^{-1}$$

We can work this same trick of subdividing a reaction into a bond-breaking stage followed by a bond-making stage for the general case of any gaseous reaction. In the first stage all the bonds joining the atoms in the reactant molecules are broken and a set of gaseous atoms results. For this stage

$$\Delta H_I = \sum_{\text{bonds broken}} D$$

The enthalpy change is the sum of the bond enthalpies for all bonds broken. In the second stage these gaseous atoms are reconstituted into the product molecules. For this second stage therefore

$$\Delta H_{II} = -\sum_{\text{bonds formed}} D$$

where the negative sign is necessary because the *reverse* of bond breaking is occurring in this stage. The total enthalpy change for the reaction at standard pressure is thus

$$\Delta H^o = \Delta H_I + \Delta H_{II}$$

or

$$\Delta H^o = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$$

The use of this equation is illustrated in the next example.

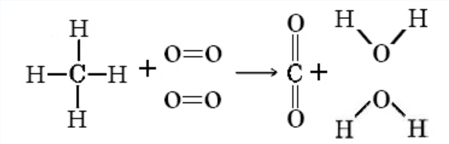
✓ Example 10.9.1: Enthalpy Change

Using Table 10.9.1 calculate the value of $\Delta H°(298\text{ K})$ for the reaction

$$\text{CH}_4(g) + 2\,\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\,\text{H}_2\text{O}(g)$$

Solution

It is best to sketch the molecules and their bonds in order to make sure that none are missed.



Thus $\Delta H^o = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$

\(= 4 D_{C\bond{-}H} + 2 D_{D\bond{=}D} - 2 D_{C\bond{=}O} - 4 D_{O\bond{-}H}\)

$$= (4 * 416 + 2 * 498 - 2 * 803 - 4 * 467)\text{kJ mol}^{-1}$$

$$= -814\text{kJ mol}^{-1}$$

The experimental value for this enthalpy change can be calculated from standard enthalpies of formation. It is –802.4 kJ mol^{-1}. The discrepancy is due to the unavoidable use of *mean* bond enthalpies in the calculation.

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