BOND ENERGY

Bond length and bond energy are used to explain molecular properties. Bond energies are useful for predicting whether a reaction will be endothermic or exothermic. When the standard enthalpy change for a reaction cannot be measured, an approximate value can be obtained by using average standard bond enthalpies. During a reaction, energy must be supplied to break bonds in the reactants, and energy is given out when the bonds in the products form.

The **bond dissociation energy, D,** is *the enthalpy change for breaking a bond in a molecule with the reactants and products in the gas phase under standard conditions.*
For the diatomic molecule XY, the bond dissociation energy is defined as the enthalpy change for the process: $XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)}$

The greater the π -bond character (i.e multiple bonds), then the shorter the bond and greater the bond energy. Suppose you wish to break the carbon-carbon bonds in ethane, $CH_3 - CH_3$, in ethene, $CH_2 = CH_2$, and in ethyne, $CH \equiv CH$. The ethane C - C bond is the longest of the series, and the ethyne, $C \equiv C$ bond is the shortest, bond breaking requires the least energy for ethane and the most energy for ethyne.

$$\text{Molecule} \underset{\text{energy released}}{\overset{\text{energy supplied}}{\rightleftarrows}} \text{Molecular Fragment}$$

The process of breaking bonds in a molecule is always endothermic. The amount of energy supplied to break carbon-carbon bonds in the molecules must be the same as the amount of energy released when the same bonds form. *The formation of bonds from atoms or radicals in the gas phase is always exothermic.*
Example: $H_{2(g)} \longrightarrow 2\,H_{(g)} \quad \Delta H^0 = D\,(H - H) = +453.9\ kJ\ mol^{-1}$

The **Table 10** in the Data Book, of Bond Enthalpies listed are all *positive.* They are the energies required to break one mole of the bond in question. If you need the energy released when one mole of bonds is formed, the magnitude is the same, but the sign is *negative.*
Example: $2\,H_{(g)} \longrightarrow H_{2(g)} \quad \Delta H^0 = D\,(H - H) = -453.9\ kJ\ mol^{-1}$

The energies are *average bond energies.* For example, a C - H bond has an average energy of 412 kJ mol^{-1}. This value may vary however, as much as 30 to 40 kJ mol^{-1} from molecule to molecule, however, just as bond lengths vary from one molecule to another.

Bond energies are defined in terms of gaseous atoms or molecular fragments. If a reactant is in the solid or liquid state, you must include the energy required to convert it to a gas before using the bond energy values.
For example, to know the energy required to convert liquid bromine to bromine atoms in the gas phase, we must first find the energy to convert liquid bromine to bromine vapour and then add on the energy required to break one mole of bromine-bromine bonds.

liquid –> vapour	$Br_{2(l)} \longrightarrow Br_{2(g)}$	$\Delta H = +30.9$ kJ
Bond Breaking	$Br_{2(g)} \longrightarrow 2\,Br_{(l)}$	$\Delta H = +192$ kJ
Total Energy	$Br_{2(l)} \longrightarrow 2\,Br_{(g)}$	$\Delta H = +232$ kJ

In reactions between molecules, bonds in the reactants are broken and new bonds are formed in the products. If the total energy released when new bonds are formed exceeds the energy required to break the original bonds, the overall reaction is exothermic. If the opposite is true, then the overall reaction is endothermic.

In general if strong bonds in reactants are broken and weak bonds in products are formed, then $\Delta H > 0$ i.e an endothermic reaction, conversely if weak bonds in reactants $\longrightarrow$ strong product bonds, then $\Delta H < 0$, an exothermic reaction.

Natural oils can be converted to fats by a reaction called a *hydrogenation,* the addition of hydrogen. A simple example of this kind of reaction is the conversion of the hydrocarbon propene to propane.

$$\underset{\text{propene}}{CH_3\,CH=CH_{2\,(g)}} \quad + \quad H\text{-}H_{(g)} \quad \dashrightarrow \quad \underset{\text{propane}}{CH_3\;\;CH_2\text{-}CH_{2\,(g)}}$$

We can use bond energies to *estimate* the enthalpy change for the reaction. The first step is to examine the reactants and product to see what bonds are broken and what bonds are formed. For the reaction in question one C - C bond and six C - H bonds are *not* changed. Thus we need to focus only on the affected bonds.

Bonds broken: 1 mol of C - C bonds and 1 mol of H - H bonds
Energy required = 611 kJ for C - C bonds + 436 kJ for H - H bonds = 1047 kJ

Bonds formed: 1 mol of C - C bonds and 2 mol of C - H bonds
Energy evolved = 347 kJ for C - C bonds + 2 mol (414 kJ/mol for C - H bonds)
= 1175 kJ

When using bond energies to find the enthalpy change for a reaction, you should add up the energies of all the bonds broken and subtract from this the sum of the energies of the bonds formed. Thus, the **standard enthalpy of reaction is the difference between the sum of the average standard bond enthalpies of the products and the sum of the average standard bond enthalpies of the reactants**:

$$\boldsymbol{\Delta H^0_{rxn} \;=\; \Sigma\; D\,(\text{bonds broken}) \;-\; \Sigma\; D\,(\text{bonds formed})}$$

This equation tells you to multiply the bond energy for each bond broken by the number of bonds of that type, and add all of these up. Then, multiply the bond energy for each bond formed by the number of bonds of that type, and add all of these up.

Because bond formation is exothermic, the quantity ''Σ D(bonds formed)'' is subtracted from the quantity ''Σ D(bonds broken).'' Therefore, for the hydrogenation reaction, we have:

$$\Delta H^0_{rxn} = 1047\text{ kJ} - 1175\text{ kJ} = -128\text{ kJ}$$

and the overall reaction is exothermic.

(Using enthalpies of formation for the propene and propane example above, we calculated $\Delta H^0_{rxn} = -123.8$ kJ, indicating that bond energy calculations can give acceptable results in many cases.)

Using Bond Energies

Acetone, a common industrial solvent, can be converted to propan-2-ol, rubbing alcohol, by hydrogenation.

$$CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3 \quad + \quad H\text{-}H \quad \dashrightarrow \quad CH_3-\underset{\underset{\Large H}{|}}{\overset{\overset{\Large O-H}{|}}{C}}-CH_3$$

Predict the enthalpy change for the reaction using bond energies.

Solution

The first step is to examine the reactants and product to see what bonds are broken and what bonds are formed. For this reaction the two C - C bonds and six C - H bonds are not changed. We therefore need only focus on the bonds that have been broken in the reactants or formed in the products.

Bonds broken: 1 mol of C=O bonds and 1 mol of H - H bonds
Energy required = 745 kJ for C=O bonds + 436 kJ for H - H bonds = 1181 kJ mol^{-1}

Bonds formed: 1 mol of C-H bonds + 1 mol of C- O bonds + 1 mol of O - H bonds
Energy evolved = 414 kJ for C - H + 351 kJ for C - O + 464 kJ for O - H = 1229 kJ mol^{-1}

$$\Delta H^0_{rxn} = \Sigma\; D\,(\text{bonds broken}) - \Sigma\; D\,(\text{bonds formed})$$
$$= 1181\text{ kJ} - 1229\text{ kJ} = -48\text{ kJ}$$