# Thermodynamics

**Unit 16A:** Thermodynamics Review - Enthalpy

### Skills:

* calculate ΔHrxn from bond enthalpies
* calculate ΔHrxn from  data

### Notes:

chemical bond: when two atoms are joined through the sharing of electrons. (We can say this because no bond is 100% ionic—even CsF has a small amount of covalent character.)

Any chemical bond that actually forms is *always* more stable than the corresponding unbonded atoms. If the bond were less stable than the unbonded atoms, the bond would fail to form.

enthalpy: stored (potential) chemical energy in the form of heat. In thermodynamics, we use the variable *H* to represent enthalpy.

state function: a function (variable) whose value depends only on the current state of the system, and whose value is independent of the pathway. Enthalpy is an example of a state function.

In thermodynamics, variables representing state functions are represented by capital letters.

## Bond Dissociation Energies

“Bond energy” is the energy required to break a chemical bond. Generally, bond dissociation energies are for homolytic dissociation (*i.e.,* the electrons are equally split between the two atoms). Heterolytic bond dissociation energies are always higher.

Here are some common heterolytic bond dissociation energies:

|  |  |
| --- | --- |
| Bond | Bond Dissociation Energy |
| C−C | 346 |
| C=C | 602 |
| C≡C | 835 |
| C−H | 411 |
| C−O | 358 |
| C=O | 799 |
| O=O | 494 |
| O−H | 459 |

You can use bond dissociation energies to determine the enthalpy change of a chemical reaction. For example, consider the combustion of methane:

CH4 + 2 O2 → CO2 + 2 H2O

This actually means:

 + 2  →  + 2 

break 4 C−H bonds + 2 O=O bonds → form 2 C=O bonds + 4 O−H bonds

By convention, energy is positive if we put it in (endothermic), and negative if it comes out (exothermic). This means the enthalpy needed to break a bond is positive, and the enthalpy released by forming a bond is negative.

Adding the energies of all of the bonds broken and formed in the equation gives the following:



## Enthalpy of Formation

The enthalpy of formation () of a compound is the Δ*H*rxn for the formation of a compound from its elements in their natural state. For Δ*Hf* values measured/calculated at “standard state” (usually defined to be 1 atm and 25°C), we add a superscript °.

The enthalpy of formation of any pure element in its natural state is defined to be zero.

For example:

2 Al (s) + 3 O2 (g) → Al2O3 (s) 

Because  for Al (s) is 0, and  for O2 (g) is also 0, this means

 for Al2O3 (s) = 

## Calculating Δ*H*rxn from Enthalpy of Formation Data

Rather than calculate  values from bond energies, it is much more convenient to look them up in a table. Thus, for the reaction:

CH4 (g) + 2 O2 (g) → CO2 (g) + 2 H2O (g)

we could simply look up the  values for each of the compounds:

|  |  |
| --- | --- |
| Compound |  |
| CH4 (g) | −74.8 |
| O2 (g) | 0 |
| CO2 (g) | −393.5 |
| H2O (g) | −241.8 |

Then:

