Enthalpies of Formation

Using Hess's Law we can calculate reaction enthalpies for a variety of reactions using tables of known enthalpies

Many experimentally determined enthalpies are listed by the type of process

DH for converting various liquids to the gas phase are listed in tables of enthalpies of vaporization

DH for melting solids to liquids are listed in tables of enthalpies of fusion

DH for for combusting a substance in oxygen are listed in tables of enthalpies of combustion

The enthalpy change associated with the formation of a compound from its constituent elements is called the enthalpy of formation (DHf)

Conditions which influence enthalpy changes include:

temperature

pressure

state of reactants and products (s, g, l, aq)

The standard state of a substance is the form most stable at 298 °K (25 °C, or standard "room temperature") and 1 atmosphere (1 atm) of pressure

When a reaction occurs with all reactants and products in their standard states, the enthalpy change is the standard enthalpy of reaction (DH°)

Thus, the standard enthalpy of formation (DH*f) of a compound is the change in enthalpy that accompanies the formation of 1 mole of that substance from its elements, with all substances in their standard states

The standard enthalpy of formation for ethanol (C2H5OH) is the enthalpy change for the following reaction

Notes:

Elemental source of oxygen is O2 and not O because O2 is the stable form of oxygen at 25 °C and 1 atm, likewise with H2

Elemental source of carbon is specified as graphite (and not, for example, diamond) because graphite is the lowest energy form of carbon at room temp and 1 atm

Why is the O2 stoichiometry left at "1/2"? The stoichiometry of formation reactions always indicates the formation of 1 mol of product. Thus, DH°f values are reported as kJ / mole of the substance produced If C(graphite) is the lowest energy form of carbon under standard conditions, then what is the DH °f for C(graphite)?

By definition, the standard enthalpy of formation of the most stable form of any element is zero because there is no formation reaction needed when the element is already in its standard state

 $DH^{\circ}f$ for C(graphite), H2(g) and O2(g) = 0

Using enthalpies of formation (DH°f) to calculate enthalpies of reaction under standard conditions (DH°rxn)

We can determine the standard enthalpy change for any reaction (DH°rxn) by using standard enthalpies of formation (DH°f) and Hess's Law

Consider the following combustion reaction of propane:

C3H8(g) + 5O2(g) -> 3CO2(g) + 4H2O(1)

The reactants:

The standard heat of formation (DH°f) of propane gas from its elemental constituents in the standard state is 103.85 kJ/mole

 $3C(graphite) + 4H2(g) -> C3H8(g) DH^{\circ}f = -103.85 \text{ kJ}$

The standard heat of formation (DH $^{\circ}$ f) for O2(g) is zero O2(g) -> O2(g) DH $^{\circ}$ f = 0 kJ

and so...

 $5O2(g) -> 5O2(g) DH^{\circ}f = 0 kJ$

Overall, therefore, the standard heat of formation (DH °f) for the reactants is:

3C(graphite)+4H2(g)+5O2(g) -> C3H8(g)+5O2(g)

 $DH^{\circ}f = -103.85 \text{ kJ}$

The products:

The standard heat of formation (DH°f) of CO2(g) from its elemental constituents in the standard state is 393.5 kJ/mole

 $C(graphite) + O2(g) -> CO2(g) DH^{\circ}f = 393.5 kJ$

so, for 3 moles of CO2 molecules the standard heat of formation would be:

 $3C(graphite) + 3O2(g) -> 3CO2(g) DH^{\circ}f = 1180.5 kJ$

The standard heat of formation (DH°f) of H2O(l) from its elemental constituents in the standard state is 285.8 kJ/mole

and so the DH°f for 4 waters would be:

combining the DH°f for both products yields:

3C(graphite)+4H2(g)+5O2(g) -> 3CO2(g)+4H2O(l)

with DH $^{\circ}$ f = (-1180.5) + (-1143.2) = -2323.7 kJ

Let's summarize what we have determined so far:

Overall the standard heat of formation (DH°f) for the reactants is:

3C(graphite)+4H2(g)+5O2(g) -> C3H8(g)+5O2(g)

 $DH^{\circ}f = -103.9 \text{ kJ}$

Overall the standard heat of formation (DH°f) for the products is:

3C(graphite)+4H2(g)+5O2(g) -> 3CO2(g)+4H2O(l)

 $DH^{\circ}f = -2323.7 \text{ kJ}$