

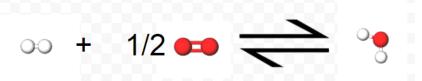
3.10: Standard Enthalpies of Formation

By now chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Fortunately Hess' law makes it possible to list a single value, **the standard enthalpy of formation** ΔH_f , for each compound. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that

$$\Delta H_f[{
m H_2O}(l)] = -285.8~{
m kJ~mol}^{-1}$$

, we can immediately write the thermochemical equation



Ball and stick structure shows a bonded pair of white spheres reacting with half of double bonded 2 red spheres to give a triangular shaped structure of red sphered bonded to two white spheres.



Macro view of the reaction between hydrogen and oxygen gas to form liquid water. Hydrogen and oxygen gas are shown in vials, glowing purple. A bed of water is shown as the product.

The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $H_2O(l)$ formed. Equation 3.10.1 must specify formation of 1 mol $H_2O(l)$, and so the coefficient of O_2 must be $\frac{1}{2}$. Note the 3 different views of this reaction, the equation providing a symbolic view, the 3D molecules providing a microscopic view, and the photos providing a macroscopic view of the reaction as we would see it with our own 2 eyes.

In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine ΔH_f . Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. A case in point is the gas acetylene, C_2H_2 . In Example 1 from the Hess' law section we showed that the thermochemical equation

$$2\mathrm{C}(s) + \mathrm{H}_2(g)
ightarrow \mathrm{C}_2\mathrm{H}_2(g) \qquad \Delta H_m = 227.0 \; \mathrm{kJ} \; \mathrm{mol}^{-1}$$

was valid. Since it involves 1 mol C_2H_2 and the elements are in their most stable forms, we can say that $\Delta H_f[C_2H_2(g)] = 227.0 \text{ kJ} \text{ mol}^{-1}$.

One further point arises from the definition of ΔH_f . The standard enthalpy of formation for an element in its most stable state must be zero. If we form mercury from its elements, for example, we are talking about the reaction

$$\mathrm{Hg}(l)
ightarrow \mathrm{Hg}(l)$$

Since the mercury is unchanged, there can be no enthalpy change, and



 $\Delta H_f = 0 \; \mathrm{kJ} \; \mathrm{mol}^{-1}$

Table 3.10.1: Some Standard Enthalpies of Formation at 25°C.

Compound	$\Delta H_f/{ m kJ}$ mol $^{-1}$	ΔH_{f} /kcal $ m mol^{-1}$	Compound	$\Delta H_f \! / \! \mathrm{kJ}$ mol $^{-1}$	ΔH _f /kcal mol ^{–1}
AgCl(s)	-127.068	-30.35	$H_2O(g)$	-241.818	-57.79
$AgN_3(s)$	+620.6	+148.3	$H_2O(l)$	-285.8	-68.3
$Ag_2O(s)$	-31.0	-7.41	$H_2O_2(l)$	-187.78	-44.86
$Al_2O_3(s)$	-1675.7	-400.40	$H_2S(g)$	-20.63	-4.93
$\mathrm{Br}_2(l)$	0.0	0.00	HgO(s)	-90.83	-21.70
$\mathrm{Br}_2(g)$	+30.907	+7.385	$I_2(s)$	0.0	0.0
C(s), graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	-436.747	-104.36
$\mathrm{CH}_4(g)$	-74.81	-17.88	KBr(s)	-393.798	-94.097
CO(g)	-110.525	-26.41	MgO(s)	-601.7	-143.77
$CO_2(g)$	-393.509	-94.05	$NH_3(g)$	-46.11	-11.02
$C_2H_2(g)$	+226.73	+54.18	NO(g)	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	-84.68	-20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	-124.7	-29.80
CaO(s)	-635.09	-151.75	NaBr(s)	-361.062	-86.28
CaCO ₃ (s)	-1206.92	-288.39	NaCl(s)	-411.153	-98.24
CuO(s)	-157.3	-37.59	$O_3(g)$	+142.7	+34.11
Fe ₂ O ₃ (s)	-824.2	-196.9	$SO_2(g)$	-296.83	-70.93
$\mathrm{HBr}(g)$	-36.4	-8.70	$SO_3(g)$	-395.72	-94.56
HCl(g)	-92.307	-22.06	ZnO(s)	-348.28	-83.22
HI(g)	+26.48	+6.33			

Standard enthalpies of formation for some common compounds are given in Table 3.10.1. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

Example 3.10.1: Change in Enthalpy

Use standard enthalpies of formation to calculate ΔH_m for the reaction

$$2\mathrm{CO}(g) + \mathrm{O}_2(g) o 2\mathrm{CO}_2(g)$$

Solution:

We can imagine that the reaction takes place in two steps, each of which involves only a standard enthalpy of formation. In the first step CO (carbon monoxide) is decomposed to its elements:

$$2{
m CO}(g)
ightarrow 2{
m C}(s) + {
m O}_2(g) \qquad \Delta H_m = \Delta H_1 \eqno(3.10.2)$$

Since this is the *reverse* of formation of 2 mol CO from its elements, the enthalpy change is



$$\Delta H_1 = 2 \times -\Delta H_f[\mathrm{CO}(g)] = 2 \times [-(-110.5 \; \mathrm{kJ} \; \mathrm{mol}^{-1})] = +221.0 \; \mathrm{kJ} \; \mathrm{mol}^{-1}$$

In the second step the elements are combined to give 2 mol CO₂(carbon dioxide):

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$$
 $\Delta H_m = \Delta H_2$ (3.10.3)

In this case

$$\Delta H_2 = 2 \times \Delta H_f[\text{CO}_2(g)] = 2 \times (-393.5 \text{ kJ mol}^{-1}) = -787.0 \text{ kJ mol}^{-1}$$

You can easily verify that the sum of Equations 3.10.2 and 3.10.3 is

$$2\mathrm{CO}(g) + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g)$$
 $\Delta H_m = \Delta H_{net}$

Therefore

$$\Delta H_{net} = \Delta H_1 + \Delta H_2 = 221.0 \; \text{kJ} \; \text{mol}^{-1} - 787.0 \text{mol}^{-1} = -566.0 \text{mol}^{-1}$$

Note carefully how Example 3.10.1 was solved. In step 1 the *reactant* compound CO(g) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_1 was opposite in sign from ΔH_f . Step 1 also involved 2 mol CO(g) and so the enthalpy change had to be doubled. In step 2 we had the hypothetical formation of the *product* CO₂(g) from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients. This can be summarized by the equation

$$\Delta H_m = \sum \Delta H_f \text{ (products)} - \sum \Delta H_f \text{ (reactants)}$$
 (3.10.4)

The symbol Σ means "the sum of." Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient derived from the equation for which ΔH_m is being calculated.

✓ Example 3.10.2: Enthalpy Change

Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction

$$4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$$

Solution

Using Equation 3.10.4, we have

$$\Delta H_m = \sum \Delta H_f \text{ (products)} - \sum \Delta H_f \text{ (reactants)}$$
 (3.10.5)

$$= [6\Delta H_f(H_2O) + 4\Delta H_f(NO)] - [4\Delta H_f(NH_3) + 5\Delta H_f(O_2)]$$
(3.10.6)

$$= 6(-241.8) \text{ kJ mol}^{-1} + 4(90.3) \text{ kJ mol}^{-1} - 4(-46.1 \text{ kJ mol}^{-1}) - 5 \times 0$$
(3.10.7)

$$= -1450.8 \text{ kJ mol}^{-1} + 361.2 \text{ kJ mol}^{-1} + 184.4 \text{ kJ mol}^{-1}$$
(3.10.8)

$$= -905.2 \text{ kJ mol}^{-1} \tag{3.10.9}$$

Note that we were careful to use $\Delta H_f[H_2O(g)]$ not $\Delta H_f[H_2O(l)]$. Even though water vapor is not the most stable form of water at 25°C, we can still use its ΔH_f value. Also the standard enthalpy of formation of the element $O_2(g)$ is zero *by definition*. Obviously it would be a waste of space to include it in the table above.

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