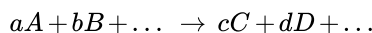


8.6: Standard Enthalpies of Reaction

The benefit of these conventions is that, **at any particular temperature**, the standard enthalpy change for a reaction

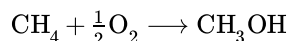


which we designate as $\Delta_r H^\circ$, is given by

$$\Delta_r H^\circ = \underbrace{c\Delta_f H^\circ(C) + d\Delta_f H^\circ(D) + \dots}_{\text{product enthalpies}} - \underbrace{a\Delta_f H^\circ(A) + b\Delta_f H^\circ(B) + \dots}_{\text{reactant enthalpies}}$$

If we have the enthalpies of formation, we can compute the enthalpy change for the reaction. We can demonstrate this by writing out the chemical equations corresponding to the formation of A, B, C, and D from their elements. When we multiply these chemical equations by the appropriately signed stoichiometric coefficient and add them, we obtain the chemical equation for the indicated reaction of A and B to give C and D. (See below.) Because enthalpy is a state function, the enthalpy change that we calculate this way will be valid for any process that converts the specified reactants into the specified products.

The oxidation of methane to methanol is a reaction that illustrates the value of this approach. The normal products in the oxidation of methane are, of course, carbon dioxide and water. If the reaction is done with an excess of methane, a portion of the carbon-containing product will be carbon monoxide rather than carbon dioxide. In any circumstance, methanol is, at best, a trace product. Nevertheless, it would be very desirable to devise a catalyst that quantitatively—or nearly quantitatively—converted methane to methanol according to the equation



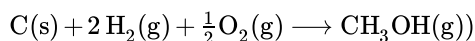
(This is frequently called a **selective oxidation**, to distinguish it from the **non-selective oxidation** that produces carbon dioxide and water.)

If the catalyst were not inordinately expensive or short-lived, and the operating pressure were sufficiently low, this would be an economical method for the manufacture of methanol. (Methanol is currently manufactured from methane. However, the process involves two steps and requires a substantial capital investment.) If the cost of manufacturing methanol could be decreased sufficiently, it would become economically feasible to convert natural gas, which cannot be transported economically unless it is feasible to build a pipeline for the purpose, into liquid methanol, which is readily transported by ship. (At present, the economic feasibility of marine transport of liquefied natural gas, LNG, is marginal, but it appears to be improving.) This technology would make it possible to utilize the fuel value of known natural gas resources that are presently useless because they are located too far from population centers.

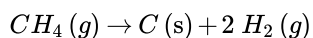
When we contemplate trying to develop a catalyst and a manufacturing plant to carry out this reaction, we soon discover reasons for wanting to know the enthalpy change. One is that the oxidative manufacture of methanol will be exothermic, so burning the methanol produced will yield less heat than would be produced by burning the methane from which it was produced. We want to know how much heat energy is lost in this way.

Another reason is that a manufacturing plant will have to control the temperature of the oxidation reaction in order to maintain optimal performance. (If the temperature is too low, the reaction rate will be too slow. If the temperature is too high, the catalyst may be deactivated in a short time, and the production of carbon oxides will probably be excessive.) A chemical engineer designing a plant will need to know how much heat is produced so that he can provide adequate cooling equipment.

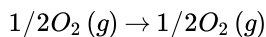
Because we do not know how to carry out this reaction, we cannot measure its enthalpy change directly. However, if we have the enthalpies of formation for methane and methanol, we can compute this enthalpy change:



$$\Delta H = \Delta_f H^\circ(\text{CH}_3\text{OH}, \text{g})$$

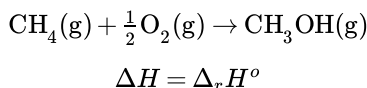


$$\Delta H = -\Delta_f H^\circ(\text{CH}_4, \text{g})$$



$$\Delta H = -\frac{1}{2}\Delta_f H^\circ(\text{O}_2, \text{g}) = 0$$

Summing the reactions gives



and summing the enthalpy changes gives

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{CH}_3\text{OH}, \text{g}) - \Delta_f H^\circ(\text{CH}_4, \text{g}) - 1/2 \Delta_f H^\circ(\text{O}_2, \text{g})$$

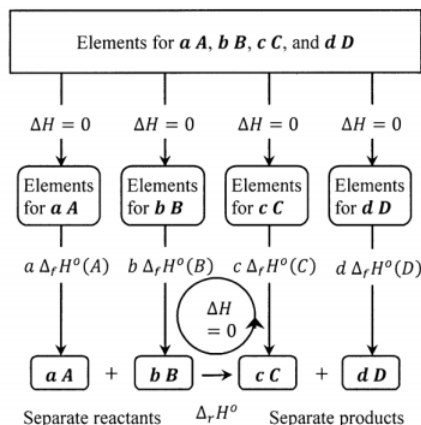


Figure 2. A thermochemical cycle to find $\Delta_r H^\circ$.

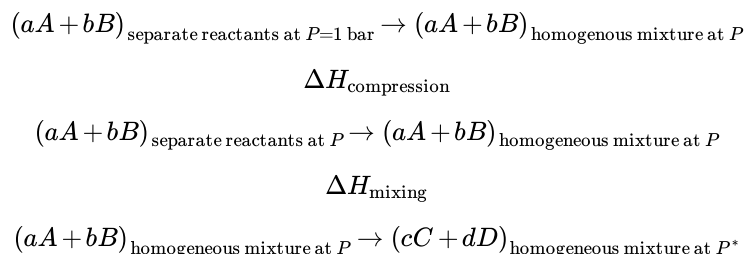
The diagram in Figure 2 shows how these conventions, and the fact that enthalpy is a state function, work together to produce, for the reaction $aA + bB + \dots \rightarrow cC + dD + \dots$, the result that the standard reaction enthalpy is given by

$$\Delta_r H^\circ = c \Delta_f H^\circ(C) + d \Delta_f H^\circ(D) + \dots - a \Delta_f H^\circ(A) - b \Delta_f H^\circ(B) - \dots$$

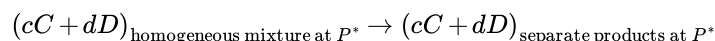
This cycle highlights another aspect of the conventions that we have developed. Note that $\Delta_r H^\circ$ is the difference between the enthalpies of formation of the **separated** products and the enthalpies of formation of the **separated** reactants. We often talk about $\Delta_r H^\circ$ as if it were the enthalpy change that would occur if we mixed a moles of A with b moles of B and the reaction proceeded quantitatively to yield a mixture containing c moles of C and d moles of D . This is usually a good approximation. However, to relate rigorously the standard enthalpy of reaction to the enthalpy change that would occur in a real system in which this reaction took place, it is necessary to recognize that there can be enthalpy changes associated with the pressure–volume changes and with the processes of **mixing** the reactants and **separating** the products.

Let us suppose that the reactants and products are gases in their hypothetical ideal-gas states at 1 bar, and that we carry out the reaction by mixing the reactants in a sealed pressure vessel. We suppose that the reaction is then initiated and that the products are formed rapidly, reaching some new pressure and an elevated temperature. (To be specific, we could imagine the reaction be the combustion of methane. We would mix known amounts of methane and oxygen in a pressure vessel and initiate the reaction using an electrical spark.) We allow the temperature to return to the original temperature of the reactants; there is an accompanying pressure change.

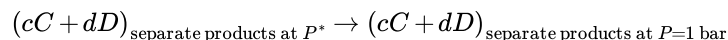
Experimentally, we measure the heat evolved as the mixed reactants are converted to the mixed products, at the original temperature. To complete the process corresponding to the standard enthalpy change, however, we must also separate the products and bring them to a pressure of 1 bar. That is, the standard enthalpy of reaction and the enthalpy change we would measure are related by the following sequence of changes, where the middle equation corresponds to the process whose enthalpy change we actually measure.



$$\Delta H_{\text{measured}}$$

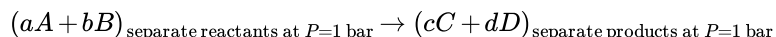


$$\Delta H_{\text{separation}}$$



$$\Delta H_{\text{expansion}}$$

Summing the reaction equations gives



$$\Delta_r H^\circ$$

and summing the enthalpy changes for the series of steps gives the standard enthalpy change for the reaction:

$$\Delta_r H^\circ = \Delta H_{\text{compression}} + \Delta H_{\text{mixing}} + \Delta H_{\text{measured}} + \Delta H_{\text{separation}} + \Delta H_{\text{expansion}}$$

It turns out that the enthalpy changes for the compression, mixing, separation, and expansion processes are usually small compared to $\Delta_r H^\circ$. This is the principal justification for our frequent failure to consider them explicitly. For ideal gases, these enthalpy changes are **identically** zero. (In [Chapter 13](#), we see that the **entropy** changes for the mixing and separation processes are important.)

When we call $\Delta_r H^\circ$ the standard enthalpy change “for the reaction,” we are indulging in a degree of poetic license. Since $\Delta_r H^\circ$ is a computed difference between the enthalpies of the pure products and those of the pure reactants, the corresponding “reaction” is a purely formal change, which is a distinctly different thing from the real-world process that actually occurs.

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