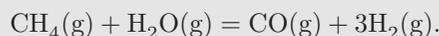


Example 14.2: Standard Enthalpy of Reaction

Steam reforming is an important industrial reaction in which natural gas, which is mostly methane, is used to produce hydrogen by reaction with water:



The reaction requires high temperatures ($\sim 800^\circ\text{C}$) and the use of catalysts. Calculate the standard enthalpy of reaction at 25°C and determine whether it is exothermic or endothermic.

Solution We construct the table below using tabulated values of the standard enthalpy of formation

	$\text{CH}_4(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{CO}(\text{g})$	$\text{H}_2(\text{g})$	
ν_i	-1	-1	1	3	
H_i°	-74,520	-241,818	-110,525	0	(J/mol)

The standard enthalpy of the reaction at 25°C is

$$\Delta H^\circ = (-1)(-74,520) + (-1)(-241,818) + (1)(-110,525) + (3)(0) = 205,813 \text{ J.}$$

This value is positive, therefore, the reaction is endothermic.

Comments The value of the standard enthalpy of reaction depends on the stoichiometry adopted, and for this reason, the stoichiometry should be indicated when the enthalpy is reported. To avoid ambiguities, the result could be reported as “205,813 J per mole of methane reacted,” or as “68,604 J per mol of hydrogen produced.”

The formation enthalpy of water is usually reported for both the gas and the liquid standard state. The correct value is the one that matches the standard state in the reaction as given in the problem statement, in this case, *g*. Notice that this is a *hypothetical* state since pure water at 1 bar, 25°C is liquid.

NOTE**Standard Enthalpy of Reaction**

The standard enthalpy of reaction should be understood as a calculation between two very specific states, that of the pure reactants before reactions, and the pure products after reaction. The calculation can be visualized as a process, as shown schematically in Figure 14-1 for the water-gas shift reaction. The pure reactants, methane and water in the ideal-gas state at 25°C and 1 bar, are mixed, possibly compressed, and heated to reaction temperature. The products are cooled and separated to be delivered as pure gases at 25°C , 1 bar. The standard enthalpy corresponds to the difference between states *A* and *G*. Since we are dealing with a state function, the enthalpy of reaction depends only on the end states but is independent of the internal details of the process.

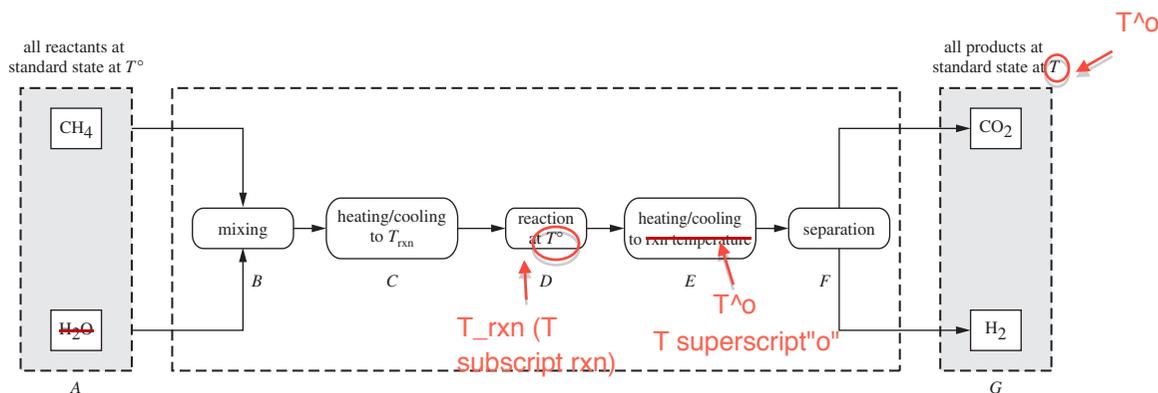


Figure 14-1: Path for the calculation of standard enthalpy of reaction.

Effect of Temperature on Enthalpy of Reaction

As we have seen, the standard enthalpy of any reaction at 25 °C may be calculated from tabulated values of the enthalpy of formation. If the enthalpy is needed at a different temperature, it can be easily calculated from its value at 25 °C. The calculation is done according to the following path:

1. Begin with all reactants at their standard state at T and calculate the enthalpy change to bring each reactant to its standard state at 25 °C (ΔH_1).
2. Calculate the standard enthalpy of reaction at 25 °C (ΔH_{298}°). This calculation delivers the products in their standard state at 25 °C.
3. Calculate the enthalpy change to bring the products from their standard state at 25 °C to their standard state at temperature T (ΔH_3).

The total change is

$$\Delta H^\circ(T) = \Delta H_1 + \Delta H_{298}^\circ + \Delta H_3.$$

The enthalpy change for step 1 is⁴

$$\Delta H_1 = \left(\sum_i \int_T^{298} |\nu_i| C_{P_i}^\circ dT \right)_{\text{reactants}} = \left(\sum_i \int_{298}^T \nu_i C_{P_i}^\circ dT \right)_{\text{reactants}}.$$

where $C_{P_i}^\circ$ is the heat capacity of species i in its standard state, $|\nu_i|$ is the absolute value of its stoichiometric coefficient, and the summation runs only through

4. To obtain the result in the far right, change the order of the limits in ΔH_1 . This brings a minus sign out which we use to write $-|\nu_i| = \nu_i$, since ν_i for the products is negative.