

Standard States

In any thermochemical equation, the states of all reactants and products must be specified; otherwise it becomes difficult for scientists to understand the experimental results of other scientists and besides there is no way get the absolute values. Defining the standard state is nothing but unifying the system. The standard state is also known as the reference point or state. Say for instance, when you measure your height, you stand up on a floor and measure your height starting from the floor with some kind of measuring device. Here, your standard or reference point is the floor. The measuring device you are using is also a standard device that is standardized against some reference point.

In thermodynamics, the standard or the reference state is 1 atm pressure for gas, 1 M concentration for solution, pure form for liquid and solid, and 25⁰ C (298 K) for temperature.

Standard Enthalpy of formation

Standard enthalpy of formation of a substance is defined as the *heat absorbed or released when one mole of a substance is formed from its most stable elements in standard states*. The reason for choosing the elements is because substances are formed by the elements. The standard enthalpy of formation is given by a symbol, ΔH_f^0 . Here superscript, ⁰, indicates the standard state and subscript, f, stands for formation.

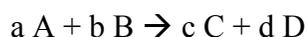
The most stable elements are assigned zero enthalpy change, i.e., $\Delta H_f^0=0$, because we do not know how much heat is involved when the elements are formed. Standard enthalpies of formation of some substances are given in the following table. For more substance you may refer to any standard general chemistry textbook.

Substance	ΔH_f^0 (kJ/mol)	Substance	ΔH_f^0 (kJ/mol)
Ag(s)	0	H ₂ O(l)	-285.83
AgCl(s)	-127.04	H ₂ O(g)	
Br ₂ (l)	0	H ₂ O ₂ (l)	-187.6
HBr(g)	-36.2	Hg(l)	0
C(graphite)	0	I ₂ (s)	0
C(diamond)	1.90	HI(g)	25.94
Cl ₂ (g)	0	N ₂ (g)	0
CH ₄ (g)	-74.81	NH ₃ (g)	-46.3
C ₂ H ₆ (g)	-84.68	NO(g)	90.4
C ₃ H ₆ (g)	-103.85	NO ₂ (g)	33.85
C ₄ H ₁₀ (g)	-124.73	O ₂ (g)	0
CH ₃ OH(l)	-238.66	O ₃ (g)	142.2
C ₂ H ₅ (l)	-277.69	S(rhombic)	0
CO(g)	-110.52	S(monoclinic)	0.30
CO ₂ (g)	-393.51	SO ₂ (g)	-296.1
H ₂ (g)	0	SO ₃ (g)	-395.2
HCl(g)	-92.3	H ₂ S (g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-347.98

Notice that some enthalpy changes are positive and some are negative. Positive value indicates an endothermic reaction and negative value indicates an exothermic reaction when a substance is formed from its elements. Also, graphite and carbon are *allotropic* (two or more forms of the same element that have different chemical and physical properties) forms of carbon. Among these, graphite is more stable than diamond, so graphite is assigned $\Delta H_f^0 = 0$. Similarly, the molecular oxygen (O_2) is more stable than its allotropic form ozone (O_3), and hence O_2 is assigned $\Delta H_f^0 = 0$. Also, sulfur in rhombic form is more stable than its allotropic form monoclinic, and therefore, rhombic form is assigned $\Delta H_f^0 = 0$.

Standard Enthalpy of Reaction

The importance of standard enthalpies of formation is to calculate the **standard enthalpy of reaction**, denoted by a symbol, $\Delta H_{\text{reaction}}^0$, or ΔH_{rxn}^0 that is defined as *the enthalpy of a reaction carried out under standard conditions*. Let us consider the following general reaction and write the enthalpy of reaction:



where a, b, c, and d are number of moles or also known as stoichiometric coefficients. The ΔH_{rxn}^0 is given by

$$\Delta H_{\text{rxn}}^0 = [c \times \Delta H_f^0(C) + d \times \Delta H_f^0(D)] - [a \times \Delta H_f^0(A) + b \times \Delta H_f^0(B)]$$

This equation can be put into a more general form:

$$\Delta H_{\text{rxn}}^0 = [\text{Sum of enthalpies of formation of Products}] - [\text{Sum of enthalpies of formation of Reactants}]$$

To calculate ΔH_{rxn}^0 , the only requirement is that ΔH_f^0 should be available in the literature for all the substances participating in a chemical reaction that of course depends upon whether we can carry out that reaction or not. If we can carry out the reaction, it is a simple matter to compute ΔH_{rxn}^0 from ΔH_f^0 (Direct Calculation). If not, we have to use Hess's law to compute ΔH_{rxn}^0 (Indirect Calculation).

Important to Remember

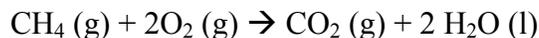
Enthalpy of formation (ΔH_f^0) applies to substances where as enthalpy of reaction (ΔH_{rxn}^0) applies to chemical reactions. Since chemical reactions involve substances, ΔH_f^0 are used to calculate ΔH_{rxn}^0 .

Direct Calculation

In this method, you use the standard enthalpies of formation of substances from the literature, i.e., tabulated values.

Example

Calculate the enthalpy of reaction for



Answer

First you write an expression for ΔH_{rxn}^0 as

$$\Delta H_{\text{rxn}}^0 = [1 \text{ mol} \times \Delta H_{\text{f}}^0(\text{CO}_2(\text{g})) + 2 \text{ mol} \times \Delta H_{\text{f}}^0(\text{H}_2\text{O}(\text{l}))] \\ - [1 \text{ mol} \times \Delta H_{\text{f}}^0(\text{CH}_4(\text{g})) + 2 \text{ mol} \times \Delta H_{\text{f}}^0(\text{O}_2(\text{g}))]$$

Now you substitute ΔH_{f}^0 values from the table and solve for ΔH_{rxn}^0 , which is shown below.

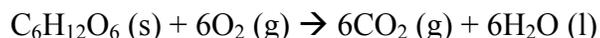
$$\Delta H_{\text{rxn}}^0 = [1 \text{ mol} \times -393.5 \text{ kJ/mol} + 2 \times -285.8 \text{ kJ/mol}] \\ - [1 \text{ mol} \times -74.81 \text{ kJ/mol} + 2 \times 0 \text{ kJ/mol}] \\ = -965.1 \text{ kJ} - (-74.81 \text{ kJ}) = -890.29 \text{ kJ}$$

By the sign on ΔH_{rxn}^0 , you can see that this reaction is an exothermic reaction.

In the above example, the enthalpy of reaction (ΔH_{rxn}^0) is calculated knowing the enthalpies of formation (ΔH_{f}^0). However, you can also calculate the enthalpy of formation (ΔH_{f}^0) knowing the enthalpy of reaction (ΔH_{rxn}^0) as illustrated in the following example.

Example

The oxidation of glucose to carbon dioxide gas and water is given by the following equation.



If the enthalpy of reaction (ΔH_{rxn}^0) is -2821.8 kJ/mol , calculate the standard enthalpy of formation of glucose.

Answer

The ΔH_{rxn}^0 is expressed by

$$\Delta H_{\text{rxn}}^0 = [6 \text{ mol} \times \Delta H_{\text{f}}^0(\text{CO}_2(\text{g})) + 6 \text{ mol} \times \Delta H_{\text{f}}^0(\text{H}_2\text{O}(\text{l}))] \\ - [1 \text{ mol} \times \Delta H_{\text{f}}^0(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \text{ mol} \times \Delta H_{\text{f}}^0(\text{O}_2(\text{g}))]$$

$$-2821.8 \text{ kJ/mol} = [6 \text{ mol} \times -393.5 \text{ kJ/mol} + 6 \text{ mol} \times -285.8 \text{ kJ/mol}] \\ - [1 \text{ mol} \times \Delta H_{\text{f}}^0(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \text{ mol} \times 0 \text{ kJ/mol}]$$

Therefore

$$\Delta H_f^0(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) = -1268.2 \text{ kJ/mol}$$

which is of course is the exothermic process.

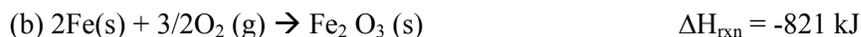
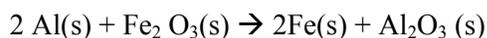
Indirect Calculation

As mentioned earlier, if the reaction cannot be carried out or difficult to carry out in the laboratory, the **Hess's law of heat summation** or simply **Hess's law** is utilized in estimating the enthalpy of reaction. This law is named after its inventor, Swiss chemist Germain Hess, that is stated as, *the change in enthalpy of reaction is the same whether the reaction is carried out in a single step or in a series of multiple steps.*

In this type of calculation, usually one main equation (for which we want to calculate ΔH_{rxn}^0) and a series of related equations along with their ΔH_{rxn}^0 are given. The task here is to manipulate series of given equations to produce the main equation. While doing so, the ΔH_{rxn}^0 are also manipulated to yield the final ΔH_{rxn}^0 for the main reaction.

Example

Consider the following reaction. Calculate the enthalpy of reaction and state whether the reaction is exothermic or endothermic.



Answer

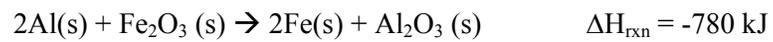
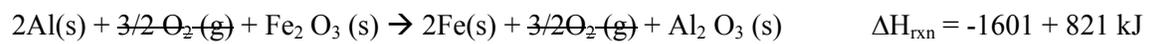
Step 1: First you reverse equation (b) to get



Step 2: Add equations (a) and (c)



Step 3: Cancel the common terms on both sides of the equation and rewrite the equation along with enthalpy.



This equation is the same as the equation in (a). Since ΔH_{rxn} is negative, it is an exothermic reaction.
