

•Standard Enthalpy of Reaction:

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar.

Standard conditions are denoted by adding the superscript \ominus to the symbol ΔH , e.g., ΔH^\ominus

•Enthalpy Changes during Phase Transformations:

1. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus} H^\ominus$.

Melting of a solid is endothermic, so all enthalpies of fusion are positive.

2. Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap} H^\ominus$.

3. Standard enthalpy of sublimation, $\Delta_{sub} H^\ominus$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar).

Sublimation is direct conversion of a solid into its vapour.

•Standard Enthalpy of Formation:

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^\ominus$.

Where the subscript ' f ' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation.

The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure.

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed.

$$\Delta_r H^\ominus = \sum a_i \Delta_f H^\ominus (\text{products}) - \sum b_i \Delta_f H^\ominus (\text{reactants})$$

where a and b represent the coefficients of the products and reactants in the balanced equation.

• Example: Decomposition of calcium carbonate.

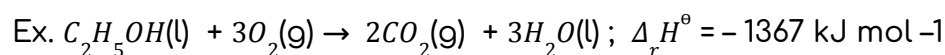


Here, a=1, b=1

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus[\text{CaO}(\text{s})] + \Delta_f H^\ominus[\text{CO}_2(\text{g})] - \Delta_f H^\ominus[\text{CaCO}_3(\text{s})] \\ &= 1(-635.1 \text{ kJ mol}^{-1}) + 1(-393.5 \text{ kJ mol}^{-1}) - 1(-1206.9 \text{ kJ mol}^{-1}) \\ &= 178.3 \text{ kJ mol}^{-1} \end{aligned}$$

• Thermochemical Equations:

A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation.



It would be necessary to remember the following conventions regarding thermo-chemical equations.

1. The coefficients in a balanced thermo-chemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.
2. The numerical value of $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ will have units as kJ mol^{-1} .

• Hess's Law of Constant Heat Summation:

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

if enthalpy of an overall reaction $\text{A} \rightarrow \text{B}$ along one route is $\Delta_r H$ and $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3, \dots$ representing enthalpies of reactions leading to same product, B along another route, then we have $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \dots$