

Chapter N° 3:
Thermochemistry

Thermochemistry is the study of the heat evolved (exothermic process) or heat absorbed (endothermic process) in chemical reactions. Thermochemistry, generally, is concerned with the heat exchange accompanying transformations, such as mixing, phase transitions, chemical reactions, etc., which include calculations of such quantities as the heat capacity, heat of combustion, heat of formation, etc.

Changing state

Changing state is the term used to describe the process of one state of matter (solid, liquid or gas) changing to another. An everyday example of this is ice melting. This is a solid (ice) changing state to become liquid (water). States of matter change when their particles either gain or lose energy; this can be due to a change in temperature. If it gets warmer, particles gain energy; if it gets colder, they lose energy. The important thing to remember is matter cannot be destroyed; it can only change. There are six changes of state possible between solids, liquids and gases:

Melting is when a solid changes to a liquid.

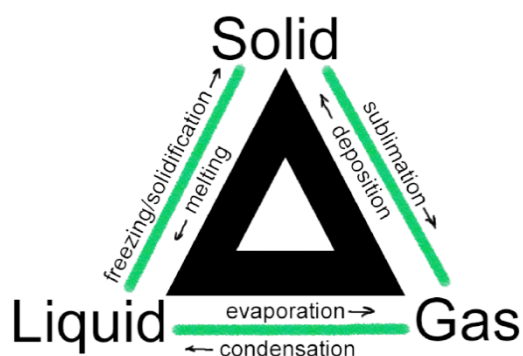
Freezing is when a liquid changes to a solid.

Evaporation (or vapourisation) is when a liquid changes to a gas.

Condensation is when a gas changes to a liquid.

Sublimation is when a solid changes to a gas.

Deposition is when a gas changes to a solid.



- If ($n_p \neq n_R$)

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + \Delta n_{(g)}RT$$

- If ($n_p = n_R$)

$$\Delta H = \Delta U$$

Types of enthalpy

$$\Delta H_{fus} = Q_{p(fus)}$$

$$\Delta H_{sol} = -\Delta H_{fus}$$

$$\Delta H_{liq} = -\Delta H_{vap}$$

The standard enthalpy of formation ΔH_f°

is the enthalpy change for the formation of 1 mol of a compound from its elements. These elements are in their standard state, which is the most stable form of the element at 1 atm and 298 K.

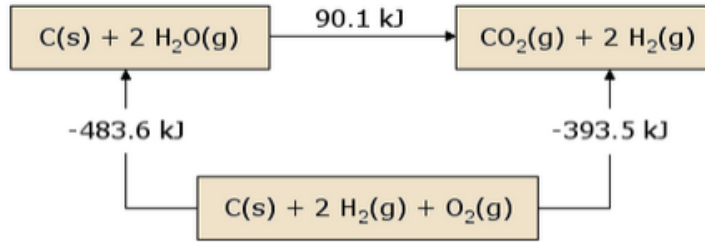
$$\Delta H_f^\circ(\text{H}_2) = \Delta H_f^\circ(\text{O}_2) = \Delta H_f^\circ(\text{N}_2) = \Delta H_f^\circ(\text{C}) = 0$$

$$\Delta H_f (\text{O}_2, \text{Cl}_2, \text{Na}, \text{Fe}) = 0$$

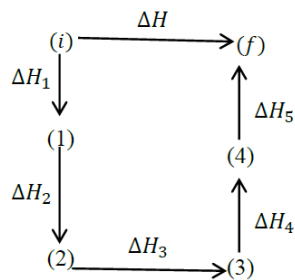
Calculate ΔH_R

By using Hess's law

A pictorial view of Hess's Law as applied to the heat of equation [2] is illustrative. In figure 1, the reactants $\text{C(s)} + 2 \text{H}_2\text{O(g)}$ are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products $\text{CO}_2\text{(g)} + 2 \text{H}_2\text{(g)}$ are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing C(s) , $\text{O}_2\text{(g)}$, and $2 \text{H}_2\text{(g)}$. This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in equation [3] and equation [4].



In general

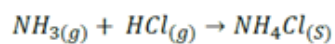


$$\Delta H_{i \rightarrow f}^f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

Determine the heat of reaction starting from the standard enthalpy of formation

Example

Calculate ΔH_R of the following reaction

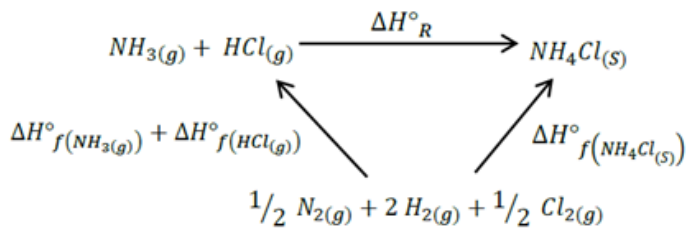


note that

$$\Delta H_f^\circ(\text{NH}_3(\text{g})) = -46,9 \text{ KJ} \cdot \text{mol}^{-1}, \quad \Delta H_f^\circ(\text{HCl}(\text{g})) = -92,3 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta H_f^\circ(\text{NH}_4\text{Cl}(\text{s})) = -314,4 \text{ KJ} \cdot \text{mol}^{-1}$$

according to hess's law



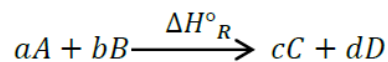
$$\Delta H^\circ_R = \Delta H^\circ_f(\text{NH}_4\text{Cl}(\text{s})) - [\Delta H^\circ_f(\text{NH}_3(\text{g})) + \Delta H^\circ_f(\text{HCl}(\text{g}))]$$

$$\Delta H^\circ_R = -314,4 - (-46,9 - 92,3) = -175,2 \text{ KJ}$$

Hess's Law

The heat of any reaction ΔH_f° for a specific reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction:

$$\Delta H^\circ_R = \sum n_p (\Delta H^\circ_f)_p - \sum n_R (\Delta H^\circ_f)_R$$



$$\Delta H^\circ_R = [c \Delta H^\circ_f(C) + d \Delta H^\circ_f(D)] - [a \Delta H^\circ_f(A) + b \Delta H^\circ_f(B)]$$

Relation between enthalpy and bond energy

$$E_d = -E_l$$

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

Kirchhoff Equation $T \neq 298\text{K}$

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta n C_p dT$$

$$\Delta U_T = \Delta U_{T_0} + \int_{T_0}^T \Delta n C_v dT$$

