Chapter III

Thermochemistry

Introduction:

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 vaporization) 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.



<u>Figure 1</u>

Types of enthalpy

Enthalpy changes phase:

Enthalpy changes phase or latent heat, energy absorbed or released by a substance during a change in its physical state (phase) that occurs without changing its temperature. The latent heat associated with melting a solid or freezing a liquid is called the **heat of fusion**; that associated with vaporizing a liquid or a solid or condensing a vapour is called the **heat of vaporization**. The latent heat is normally expressed as the amount of heat (in units of joules or calories) per mole or unit mass of the substance undergoing a change of state.

Continuous heating of pure solid results in transformations represented in the following figure 2:



Figure 2

- Enthalpy of fusion (ΔH_{fus}) (or Latent Heat of fusion): change in enthalpy due to fusion (melting) of 1 mol of a substance.
- Enthalpy of vaporization (ΔH_{vap}) (or Latent Heat of vaporization): change in enthalpy due to vaporizing (liquid to gas) of 1 mol of a substance.
- Enthalpy of condensation (ΔH_{cond}) (or Latent Heat of condensation): change in enthalpy due to condensation of 1 mol of a substance, condensation is the polar opposite of evaporation.

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

Enthalpy of solidification (ΔH_{solid}) (or Latent Heat of solidification): change in enthalpy due to solidification (freezing) of 1 mol of a substance.

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

• 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. Here is an example:

 $C + O2 \rightarrow CO2 \Delta H^{\circ}_{f} = -393.5 \text{ kJ/mol}$

Here is a table of some common standard enthalpies of formation:

Compound	ΔH^{o}_{f} (kJ/mol)
CO _(g)	-393.5
$H_2O_{(g)}$	-241.8
H ₂ O _(l)	-285.8
NaCl _(s)	-411.0
NH _{3 (g)}	-46.2
NO _{2 (g)}	33.9

The standard enthalpy is dependent on the state (ex: solid/liquid/gas) of the molecule. As you'll see above, the standard enthalpy for water as a liquid and as a gas is different. In addition, The heat of formation (ΔH_f°) of an element in its standard state is zero. This is because it doesn't take any energy to form a naturally occurring compound (there is no reaction). A pure element in its standard state has a standard enthalpy of formation of zero.

$$\Delta H_{f}^{\circ}(H_{2}) = \Delta H_{f}^{\circ}(O_{2}) = \Delta H_{f}^{\circ}(N_{2}) = \Delta H_{f}^{\circ}(C) = 0$$

Relation between internal energy enthalpy:

The following relation can be established between the standard enthalpy of a reaction and the variation in standard internal energy:

$$aA_{(g)} + bB_{(g)} \rightarrow cC_{(g)} + dD_{(g)}$$

 $P_1, V_1, T, \quad n_1 = a + b \qquad P_2, V_2, T, \quad n_2 = c + d$
 $U_1, H_1 \qquad U_2, H_2$

$$\begin{split} \Delta H &= H_2 - H_1 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \\ \Delta H &= \Delta U + (P_2 V_2 - P_1 V_1) \end{split}$$

We have : $P_1V_1 = n_1RT$, $P_2V_2 = n_2RT$

Compensation in the previous equation we find :

 $\Delta H = \Delta U + (n_2 RT - n_1 RT)$

$\Delta \mathbf{H} = \Delta \mathbf{U} + \Delta \mathbf{n}_{\mathbf{gRT}}$

 Δn_g calculated only for gaseous materials.

Heat of a reaction :

we have the next chemical reaction :

aA + bB	\rightarrow	cC + dD
Reactants		products

Heat of a reaction is defined as the amount of heat absorbed or evolved at a given temperature when the reactants have combined to form the products is represented by balanced chemical equation.

When the reaction evolves energy in the form of heat, it called exothermic reaction and When the reactants absorb heat energy from the surroundings to form products, the reaction called endothermic reaction.

• If the reaction happens at constant volume, the heat of the reaction called constant volume heat $Q_{\rm V}$.

$Q_V = \Delta U$

This quantity (ΔU), called the change in internal energy of reaction, is the heat of reaction at constant volume.

• If the reaction occurs at constant pressure, the heat of the reaction called heat at constant pressure Q_P.

$\mathbf{Q}_{\mathbf{P}} = \Delta \mathbf{H}$

This quantity (Δ H), called the change in enthalpy of reaction, is the heat of reaction at constant pressure.

Enthalpy of Reaction

a. **Definition** :

The enthalpy of reaction (ΔH_R) is the change in enthalpy due to a chemical reaction. If $\Delta H_R > 0$, the reaction is endothermic (the system pulls in heat from its surroundings) If $\Delta H_R < 0$, the reaction is exothermic (the system releases heat into its surroundings).

Measurement of Enthalpy of chemical reaction :

a- direct method:

The experimental technique known as calorimetry is used to assess enthalpy and internal energy in most cases. Calorimetry is based on thermometric methods that are carried out in a calorimeter that is immersed in a known volume of liquid. The heat released during the process is typically computed using known heat capacities of the liquid and temperature changes measured by the calorimeter.

b- Indirect method : Hess's law:

Hess's law, rule first enunciated by Germain Henri Hess, stating that the heat absorbed or evolved (or the change in enthalpy) in any chemical reaction is a fixed quantity and is independent of the path of the reaction or the number of steps taken to obtain the reaction. Hess's law can be written as $\Delta H^{\circ} = \Sigma \Delta H_n$, where ΔH° is the heat absorbed or evolved and $\Sigma \Delta H_n$ is the sum of the heat absorbed or evolved in the individual *n* steps of the reaction. Hess's law is a consequence of the first law of thermodynamics and need not be considered a separate thermodynamic law; in thermochemistry, however, it retains its identity because of its importance as the basis for calculating heats of reactions. In figure 3, the reactants C(s) + 2 H₂O(g) are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products $CO_2(g) + 2 H_2(g)$ 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), O₂(g), and 2 H₂(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].





Figure 4

In general

This includes, in general, all reactions: Enthalpy of chemical reaction is equal to the total standard enthalpy of formation of products minus the total standard enthalpy of formation of reactants.

$$\Delta H^{\circ}_{R} = \sum n_{p} \left(\Delta H^{\circ}_{f} \right)_{p} - \sum n_{R} \left(\Delta H^{\circ}_{f} \right)_{R}$$

$$aA + bB \xrightarrow{\Delta H^{\circ}_{R}} cC + dD$$
$$\Delta H^{\circ}_{R} = [c \Delta H^{\circ}_{f(C)} + d \Delta H^{\circ}_{f(D)}] - [a \Delta H^{\circ}_{f(A)} + b \Delta H^{\circ}_{f(B)}]$$

Example: Calculate ΔH_R° for the following reaction:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(S)}$$

We have :

$$\Delta H^{\circ}_{(NH_{3(g)})} = -46,9 \text{ KJ. mol}^{-1}, \ \Delta H^{\circ}_{(HCl_{(g)})} = -92,3 \text{ KJ. mol}^{-1}$$
$$\Delta H^{\circ}_{(NH_{4Cl})} = -314,4 \text{ KJ. mol}^{-1}$$

According to the Hess law:

$$NH_{3(g)} + HCl_{(g)} \xrightarrow{\Delta H^{\circ}_{R}} NH_{4}Cl_{(S)}$$

$$\Delta H^{\circ}_{(NH_{3(g)})} + \Delta H^{\circ}_{f(HCl_{(g)})} \xrightarrow{\Lambda} \Delta H^{\circ}_{f(NH_{4}Cl_{(S)})}$$

$$\frac{1}{2} N_{2(g)} + 2 H_{2(g)} + \frac{1}{2} Cl_{2(g)}$$

$$\Delta H^{\circ}_{R} = \Delta H^{\circ}_{(NH_{4}Cl_{(S)})} - [\Delta H^{\circ}_{f(NH_{3}(g))} + \Delta H^{\circ}_{f(HCl_{(g)})}]$$
$$\Delta H^{\circ}_{R} = -314,4 - (-46,9 - 92,3) = -175,2 \text{ KJ}$$

This includes, in general, all reactions: Enthalpy of chemical reaction is equal to the total standard enthalpy of formation of products minus the total standard enthalpy of formation of reactant

Relation between enthalpy and bond energy:

Bond enthalpy and enthalpy of reaction help us understand how a chemical system uses energy during reactions. The bond enthalpy describes how much energy is needed to break or form a bond, and it is also a measure of bond strength. By combining the bond enthalpy values for all of the bonds broken and formed during a reaction, it's possible to estimate the total change in potential energy of the system, which is ΔH_R for a reaction at constant pressure. Depending on whether the enthalpy of reaction is positive or negative, we can determine whether a reaction will be endothermic or exothermic.

Relation between enthalpy and bond energy

 $\mathbf{E}_{\mathbf{d}} = -\mathbf{E}_l$

$$\begin{split} \Delta H_f &= \Delta H_1 + \Delta H_2 = \sum E_d + \sum E_l \\ &= \sum -E_{l(\Box)} + \sum E_{l(\Box)} \\ &= \sum E_{l(\Box)} - \sum E_{l(\Box)} \\ \Delta H_f &= \sum E_{l(\Box)} - \sum E_{l(\Box)} \\ \end{split}$$

Effect of Temperature on Heat of Reaction: (The Kirchhoff

Equation)

KIRCHHOFF's law involves determining the enthalpy of reaction at a temperature different from that of the standard state.

Kirchhoff's Equation is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants. The same reaction, when carried at dissimilar temperatures, the enthalpies of reaction are also different.

We have the next chemical reaction :

$$aA + bB \to cC + dD$$
$$\Delta H_R = \sum n_p \left(\Delta H^\circ_f\right)_p - \sum n_R \left(\Delta H^\circ_f\right)_R$$
$$\Delta H_R = d\Delta H(D) + c\Delta H(C) - a\Delta H(A) - b\Delta H(B)$$

We know that :

$$C_P = \left(\frac{d\Delta H}{dT}\right)_p$$

By deriving the previous equation for T:

$$\frac{d\Delta H_R}{dT} = \frac{d}{dT} \begin{bmatrix} \sum n_p (\Delta H)_p - \sum n_R (\Delta H)_R \end{bmatrix}$$
$$= \sum n_P (produits) - \sum n_R (réactifs)$$
$$\frac{d\Delta H_R}{dT} = \Delta nC_P \dots \dots \dots \dots (1)$$
$$\Delta nC_P = dC_P(D) + cC_P(C) - aC_P(A) - bC_P(B)$$

By integrating relationship (1) we find:

$$\int_{\Delta H_{T_0}}^{\Delta H_T} d(\Delta H_R) = \int_{T_0}^T \Delta n C_P dT$$
$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta n C_P dT$$

Similarly, it may be shown that if the process is carried out at constant volume the relationship is:



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