THERMOCHEMISTRY

1. Heat or Enthalpy of reaction:

denoted as ΔH, is calculated using the equation

$$\Delta H = \Sigma H_p - \Sigma H_R.$$

For instance, consider the reaction: $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 44.0$ kcal.

The enthalpy change in this reaction is determined by the difference between the sum of the enthalpies of the products (ΣH_p) and the sum of the enthalpies of the reactants (ΣH_R).

The Enthalpy of reaction is influenced by various factors:

(a) The physical state of reactants and products plays a crucial role.

For example, the reaction $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ has a ΔH of -57.8 kcal, while the same reaction with $H_2O(l)$ as the product has a ΔH of -68.32 kcal.

(b) Allotropic forms of an element also impact enthalpy. Consider the reactions involving different forms of carbon (diamond and graphite) reacting with oxygen to form $CO_2(g)$. The enthalpy changes for C (diamond) $+ O_2(g) \longrightarrow CO_2(g)$ is -94.3 kcal, whereas for C (graphite) $+ O_2(g) \longrightarrow CO_2$ (g), it is -97.6 kcal.

(c) Enthalpies of reaction vary when comparing dry substances reacting to the same substances reacting in solution form.

For example, the reaction $H_2S(g) + L_2(g) \longrightarrow 2HI + S$ has a ΔH of -17.2 kcal, while the same reaction with H_2S in solution form has a ΔH of -21.93 kcal. This difference is indicative of the influence of the physical state of the reactants on the enthalpy change.

2. Enthalpy or heat of formation:

The Enthalpy or Heat of Formation is defined as the amount of heat either absorbed or evolved when one mole of a substance is directly produced from its constituent elements. This process can be exemplified through reactions such as:

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -97.6 \text{ kcal}$$

$$Ca(s) + \tfrac{1}{2} O_2(g) \longrightarrow CaO(s); \qquad \Delta H = -635.09 \text{ kcal}$$

In these reactions, the enthalpy change (ΔH) represents the heat involved in the formation of one mole of the respective substances directly from their elemental components.

The relationship between the enthalpy changes for a reaction ($\Delta H_{reaction}$) and the total enthalpy change (ΔH_T) can be expressed as follows:

$$\Delta H_{\text{reaction}} = \Sigma(\Delta H_1)_{\text{probuet}} - \Sigma(\Delta H_1)_{\text{reactant}}$$

This equation illustrates that the enthalpy change for a reaction is equal to the sum of the enthalpies of formation for the products, each multiplied by their respective coefficients, minus the sum of the enthalpies of formation for the reactants, also multiplied by their coefficients. This relationship allows for the calculation of the enthalpy change in a reaction based on the enthalpies of formation of the substances involved.

3. Enthalpy of Combustion

The Enthalpy of Combustion is defined as the quantity of heat liberated when one mole of a substance undergoes complete oxidation. This phenomenon can be exemplified through the combustion reaction of methane (CH_4) with oxygen (O_2), represented as:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2 + 2H_2O(l); \qquad \Delta H = -890.3 \text{ kJ mol}^{-1}$$

In this chemical reaction, one mole of methane reacts with two moles of oxygen to produce carbon dioxide (CO_2) and two moles of water (H_2O) in liquid form. The negative enthalpy change, indicated by $\Delta H = -890.3 \text{ kJ mol}^{-1}$, signifies that heat is released during the combustion process. This release of heat is a characteristic feature of combustion reactions and is attributed to the exothermic nature of the reaction, where the reactants, in this case, methane and oxygen, are converted into the products with the simultaneous liberation of energy in the form of heat.

4. Enthalpy of Solution:

The Enthalpy of Solution is defined as the quantity of heat either released or absorbed when one mole of a solute dissolves in an excess of solvent. This process is exemplified through various examples:

Dissolution of KCl (s) in water: $KCl(s) + H_2O \rightarrow KCl(aq)$; $\Delta H = +44.0$ kcal
Dissolution of HCl (g) in water: $HCl(g) + H_2O \rightarrow HCl(aq)$; $\Delta H = -39.3$ kcal
Dissolution of H_2SO_4 in water: $H_2SO_4(N) + H_2O \rightarrow H_2SO_4(aq)$; $\Delta H = -20.2$ kcal
Dissolution of KOH (s) in water: $KOH(s) + H_2O \rightarrow KOH(aq)$; $\Delta H = -13.3$ kcal

In each of these reactions, one mole of the respective solute is introduced to an excess of the solvent, leading to the formation of an aqueous solution. The enthalpy change (ΔH) indicates whether the process is endothermic (absorbing heat) or exothermic (releasing heat). Positive values signify an endothermic reaction, while negative values indicate an exothermic reaction. The Enthalpy of Solution provides insights into the heat dynamics associated with the dissolution of different solutes in a solvent.

5. Enthalpy of Neutralization:

The Enthalpy of Neutralization is characterized by the heat released during the reaction between a strong acid and a strong base, specifically in the formation of water from $H+$ and $OH-$ ions. This process is represented by the equation:

1g equivalent of a strong acid + 1g equivalent of a strong base = Salt + 1g equivalent of water; $\Delta H = -13.7$ kcal/geq

In the case of a weak acid, the enthalpy of neutralization is less than 13.7 kcal. The difference between 13.7 kcal and $\Delta H_{neutralization}$ represents the energy required to break down the weak acid. Therefore, the weaker the acid, the lower the $\Delta H_{neutralization}$. Consequently, the order of $\Delta H_{neutralization}$ is as follows:

1. Highest for strong acid-strong base neutralization.
2. Subsequently, for strong base-weak acid or weak base-strong acid neutralization.
3. Lastly, for weak acid-weak base neutralization.

This order reflects the varying energy changes associated with neutralization reactions involving different strengths of acids and bases. The Enthalpy of Neutralization provides valuable insights into the thermodynamics of these chemical reactions.

6. Enthalpy of Phase Change:

(a) Fusion:

As solid ice is heated below 273 K at an external pressure of 1 atm, its temperature gradually increases. However, when it reaches 273 K, it begins to transform into a liquid phase without a temperature rise. This phenomenon signifies a reversible phase transition from the solid to the liquid state, and it can be depicted as follows:

$$H_2O\ (s) \rightleftharpoons H_2O\ (\lambda)$$

Given that the process is reversible, it is reasonable to assume that phase transitions occurring at constant temperature and pressure are also reversible phase transitions.

$$\Delta S_{fustion} = \frac{\triangle H_{fiusion}}{T_f} \text{ entropy of fusion at Melting point.}$$

(b) Enthalpy of Vaporization:

Through your everyday observations, you're aware that under atmospheric pressure, the temperature of H_2O (liquid) cannot surpass 373 K. This limitation is due to the fact that at 373 K, liquid H_2O undergoes a phase transition.

$$H_2O\ (\lambda) \rightleftharpoons H_2O(g)$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

(c) Enthalpy of Sublimation:

It is the process in which solid directly changes into gaseous state

$$X(s) \rightleftharpoons X(g)$$

$$\Delta S_{sab} = \frac{\Delta H_{sab}}{T_{sab}}$$

7. Enthalpy of Hydration

The alteration in enthalpy occurs when a singular mole of a specified anhydrous or partially hydrated salt undergoes a combination with the appropriate quantity of water molecules, leading to the formation of a distinct hydrate.

For instance, the reaction involving $CuSO_4(s) + 5H_2O(I)$ results in the creation of $CuSO_4.5H_2O(s)$, with a corresponding enthalpy change denoted as $\Delta H = -18.69$ kcal.

8. Enthalpy of Atomization

The alteration in enthalpy associated with the process wherein a single mole of a specific substance dissociates into gaseous atoms is termed the enthalpy of atomization. To elucidate this concept, let's consider an example:

In the reaction $H_2(g) \rightarrow 2H(g)$, the enthalpy change ($\Delta_a H^{\ominus}$) is measured as 435.0 kJ mol^{-1}. This reaction illustrates the breakdown of dihydrogen into individual hydrogen atoms. As hydrogen atoms are initially bonded in dihydrogen, breaking this bond necessitates an input of energy. The enthalpy changes in breaking down one mole of bonds entirely to produce gaseous atoms is recognized as the enthalpy of atomization. In this specific case, it is also referred to as bond dissociation enthalpy.

Additional instances of enthalpy of atomization include the reaction $CH_4(g) \rightarrow C(g) + 4H(g)$, where the enthalpy change ($\Delta_a H^{\ominus}$) is noted as 1665 kJ mol^{-1}. In this reaction, the end products are solely gaseous atoms of carbon (C) and hydrogen (H).

9. Standard Enthalpy of Reactions

Since the enthalpy of a reaction is subject to variations in temperature, it becomes necessary to express the change in enthalpies for different reactions under standardized conditions for meaningful comparisons. The standard enthalpy of a system is defined as "the enthalpy change for a reaction when all participating substances are in their standard states."

The standard state of a substance is characterized as its most stable state at one bar pressure and a specified temperature. Typically, the conventional temperature for reporting standard thermodynamic data is 25°C, unless explicitly stated otherwise. This standard state condition is denoted by $\Delta_r H^{\ominus}$, where the superscript $\ominus$ to the symbol H indicates that the enthalpy is measured under standard conditions.

10. Standard Enthalpy of Formation

The standard enthalpy of formation for a substance is defined as the enthalpy change associated with the formation of one mole of a compound from its constituent elements, each in their most stable states of aggregation, also known as reference states.

This parameter is represented by $\Delta_f H^\ominus$, where the subscript 'f' indicates that one mole of the compound is formed in its standard state from its constituent elements in their most stable states of aggregation. The reference state for an element is its most stable state of aggregation at 298 K and 1 bar pressure. For instance, the reference state of dihydrogen is H_2 gas, and for dioxygen, carbon, and sulfur, it is O_2 gas, Cgraphite, and Srhombic, respectively. This ensures a consistent benchmark for comparison. Below are some examples of reactions along with their standard molar enthalpies of formation:

$C(S)_{graphite} + 2H_2(g) \rightarrow CH_4(g)$; $\Delta_f H^\ominus = -74.81 \text{ kJ mol}^{-1}$

$2C(S)_{graphite} + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$; $\Delta_f H^\ominus = -277.7 \text{ kJ mol}^{-1}$