THERMOCHEMISTRY
PART - I

B.Sc. (Hons.) CHEMISTRY
Part - II

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THERMOCHEMISTRY – I

The term "Thermochemistry" is made up from combination of two words 'Thermo' and 'Chemistry'.

$$Thermochemistry = Thermo + Chemistry$$

'Thermo' represents heat and 'Chemistry' is the study of chemical reactions. Chemical reactions are almost invariably accompanied by energy changes. These energy changes appear as evolution or absorption of heat during chemical reactions. These heat change, q may be equal to ΔH or ΔE as per state of the reaction. If reaction takes place at constant pressure then

$$q_p = \Delta H$$

If reaction takes place at constant volume then
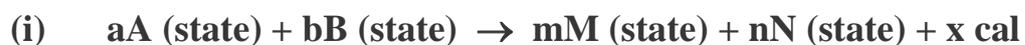
$$q_v = \Delta E$$

THERMOCHEMISTRY is the study of heat changes in chemical reactions.

Thermochemistry of a chemical reaction is represented by a Thermo-chemical equation. Thermo-chemical equation of a chemical reaction is the balanced chemical equation of the reaction with heat change involved. A thermo-chemical equation is complete and correct only when state of each of the reactants and products in the chemical reaction has been mentioned beside formula of respective reactants and products in the equation.

Exothermic Reaction: When a chemical reaction is accompanied with evolution of heat, such a chemical reaction is known as Exothermic reaction. For example, consider a chemical reaction having balanced chemical equation as

$$aA + bB \rightarrow mM + nN$$

When reaction takes place as per the balanced equation, x calories heat is evolved. Definitely, this is an exothermic reaction. Thermo-chemical equation of this exothermic reaction may be written by either of the following ways:

   (i)   aA (state) + bB (state) $\rightarrow$ mM (state) + nN (state) + x cal
   (ii)   aA (state) + bB (state) - x cal $\rightarrow$ mM (state) + nN (state)

(iii) aA (state) + bB (state) $\rightarrow$ mM (state) + nN (state) q_p = - x cal

   [As most of the chemical reactions take place at constant pressure

   q = q_p = ΔH]

(iv) aA (state) + bB (state) $\rightarrow$ mM (state) + nN (state) ΔH = - x cal

Endothermic Reaction: When a chemical reaction is accompanied with absorption of heat, such a chemical reaction is known as Endothermic reaction. For example, consider a chemical reaction having balanced chemical equation as

$$dD + eE \rightarrow fF + gG$$

When reaction takes place as per the balanced equation, y calories heat is absorbed. Definitely, this is an endothermic reaction. Thermo-chemical equation of this endothermic reaction may be written by either of the following ways:

(i) dD (state) + eE (state) + y cal $\rightarrow$ fF (state) + gG (state)

(ii) dD (state) + eE (state) $\rightarrow$ fF (state) + gG (state) – y cal

(iii) dD (state) + eE (state) $\rightarrow$ fF (state) + gG (state) q_p = + y cal

(iv) dD (state) + eE (state) $\rightarrow$ fF (state) + gG (state) ΔH = + y cal

Standard State:

A condition when pressure is 1bar ($\approx$ 1atm) and temperature is 25^0C, is called Standard State. Standard State is represented by putting (^{0}) on the state function representation.


Heat of reaction

Amount of heat evolved or absorbed in a chemical reaction as per balanced equation, is known as 'Heat of reaction'. If the reaction is carried out at constant pressure, 'Heat of reaction' is termed 'Enthalpy of reaction'.

At standard state:

Heat of reaction = Standard enthalpy of reaction = ΔH^0

UNIT: Energy or Heat unit

For example:

aA (s) + bB (l) $\rightarrow$ mM (s) + nN (g) ΔH^0 = - x J

    $\therefore$ Standard enthalpy of reaction = ΔH^0 = - x J
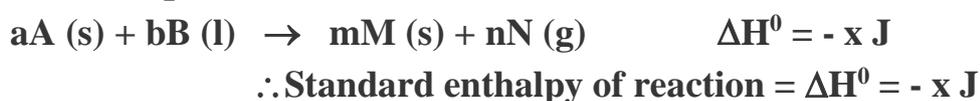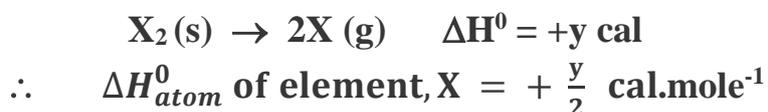
Heat of atomisation

Amount of heat required to obtain 1mole gaseous atoms from the element in its natural state, is known as 'Heat of atomisation' of the element. If this process is carried out at constant pressure. 'Heat of atomisation' is termed 'Enthalpy of atomisation'.

At standard state:

Heat of atomisation = Standard enthalpy of atomisation = ΔH^0_{atom}

UNIT: (Energy or Heat unit).mole^{-1}

For example:

$$X_2\,(s) \;\rightarrow\; 2X\,(g) \qquad \Delta H^0 = +y \text{ cal}$$

$$\therefore \quad \Delta H^0_{atom} \text{ of element, } X \;=\; + \frac{y}{2} \text{ cal.mole}^{-1}$$
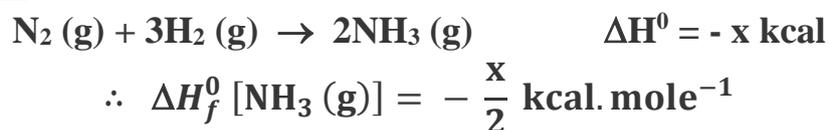
Heat of formation

Amount of heat evolved or absorbed when 1mole of a compound is formed from its constituent elements in their natural states, is known as 'Heat of formation' of that compound. If this process is carried out at constant pressure, 'Heat of formation' is termed 'Enthalpy of formation'.

At standard state:

Heat of formation = Standard enthalpy of formation = ΔH^0_f

UNIT: (Energy or Heat unit).mole^{-1}

For example:

$$N_2\,(g) + 3H_2\,(g) \;\rightarrow\; 2NH_3\,(g) \qquad \Delta H^0 = -x \text{ kcal}$$

$$\therefore \quad \Delta H^0_f\,[NH_3\,(g)] \;=\; -\frac{x}{2} \text{ kcal. mole}^{-1}$$

Heat of combustion

Amount of heat evolved when 1mole of a substance is burnt completely in presence of sufficient oxygen, i.e. substance is completely oxidised, is known as 'Heat of combustion of that substance. If this process is carried out at constant pressure, 'Heat of combustion' is termed as 'Enthalpy of combustion'.

At standard state:

Heat of combustion = Standard enthalpy of combustion $= \triangle H_C^0$

UNIT: (Energy or Heat unit).mole^{-1}

For example;

$$2C_6H_6 \text{ (g)} + 15\, O_2 \text{ (g)} \rightarrow 12CO_2 \text{ (g)} + 6H_2O \text{ (l)} \qquad \triangle H^0 = -x \text{ kcal}$$
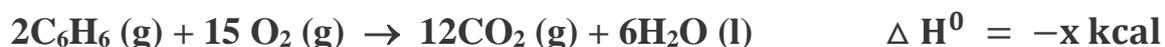
$$\triangle H_C^0\, [C_6H_6(g)] = -\frac{x}{2} \text{ kcal. mole}^{-1}$$

Heat of neutralisation

Amount of heat evolved when 1equivalent each of an acid and a base in dilute solutions are reacted for complete neutralisation, is known as 'Heat of neutralisation' for that acid – base pair. If this process is carried out at constant pressure, 'Heat of neutralisation' is termed 'Enthalpy of neutralisation'.

At standard state:

Heat of neutralisation = Standard enthalpy of neutralisation

UNIT: (Energy or Heat unit).eq^{-1}

<u>Standard enthalpy of neutralisation for a strong acid – strong base pair is always 13.7 kcal or 57.1 kJ eq^{-1}. However, in case of weak acid or weak base, Standard enthalpy of neutralisation is always less than 13.7 kcal or 57.1 kJ.eq^{-1}.</u>

Arrhenius acid – base neutralisation reaction is nothing but a reaction between H^+ and OH^-. Complete dissociation or ionization of 1eq of an acid and 1eq of a base produce 1mole H^+ ions and 1mole OH^- ions, respectively.

Therefore, complete neutralisation reaction between 1eq of an acid and 1eq of a base is a reaction between 1mole H$^+$ ions and 1mole OH$^-$ ions.

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l) \qquad \triangle H^0 = -13.7 \text{ kcal} = -57.1 \text{ kJ}$$

To obtain standard enthalpy of neutralisation, there must be complete dissociation of 1eq of acid and 1eq of base. If acid or base is partially dissociated, a part of heat of reaction between 1mole H$^+$ and 1mole OH$^-$ is used to complete dissociation process.

$$\therefore \triangle H^0 (neutralisation) = \triangle H^0 (dissociation) + \triangle H^0 (H^+ + OH^-)$$

Strong acid or strong base, as and when dissolved in water, dissociates completely. Therefore, in case of strong acid and strong base

$$\triangle H^0 (dissociation) = 0$$

Weak acid or weak base partially dissociate in water. Hence, for a weak acid or weak base

$$\triangle H^0 (dissociation) > 0$$

Thus, standard enthalpy of neutralisation for a strong acid – strong base pair is always 13.7 kcal or 57.1kJ.eq^{-1} but enthalpy of neutralisation for a weak acid or a weak base is always less than 13.7 kcal or 57.1kJ.eq^{-1}.

Heat of solution

Amount of heat evolved or absorbed when 1mole of a solute is dissolved completely in such a large excess of solvent that no further dilution produce any heat change, is known as 'Heat of solution'. If this process is carried out at constant pressure, 'Heat of solution' is termed 'Enthalpy of solution'.

<u>At standard state:</u>

Heat of solution = Standard enthalpy of solution

UNIT: (Energy or Heat unit).moie^{-1}

<u>For example:</u>

$$KOH (s) + aq \rightarrow KOH (aq) \qquad \Delta H^0 = -13.3 \text{ kcal} \therefore$$

$$\text{Standard enthalpy of solution} = \Delta H^0_{Solution} = -13.3 \text{ kcal. mole}^{-1}$$
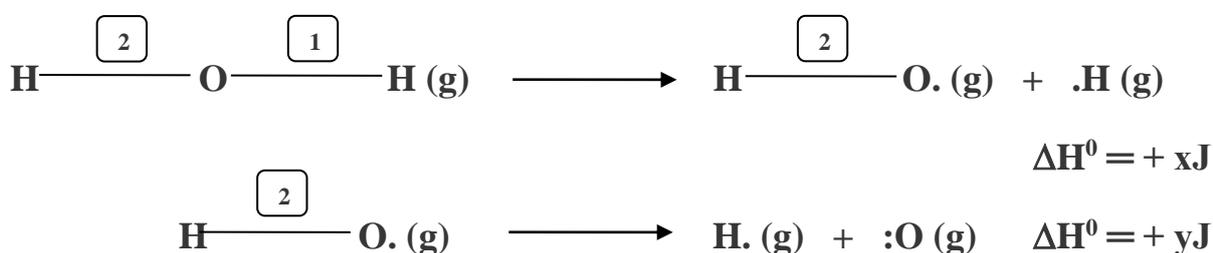
Bond Dissociation Energy & Bond Energy

Energy is required to break a chemical bond and energy is released when a chemical bond is formed. Amount of energy involved in breaking or formation of a chemical bond is same.

Energy required to break 1mole of a particular covalent chemical bond in gaseous phase is known as 'Bond dissociation energy' of that particular chemical bond. The average of bond dissociation energies of all such chemical bonds is called 'Bond Energy' for that chemical bond. When the process is carried out at standard state, 'Bond dissociation energy' and 'Bond energy' are termed as 'Bond dissociation enthalpy' and 'Bond enthalpy', respectively.

UNIT: (Energy unit).mole^{-1}

For example:

Consider H_2O molecule which consists of two O – H bonds.

$$H \overset{\boxed{2}}{\rule{1.5cm}{0.4pt}} O \overset{\boxed{1}}{\rule{1.5cm}{0.4pt}} H\ (g) \longrightarrow H \overset{\boxed{2}}{\rule{1.5cm}{0.4pt}} O.\ (g)\ +\ .H\ (g)$$

$$\Delta H^0 = + \text{xJ}$$

$$H \overset{\boxed{2}}{\rule{1.5cm}{0.4pt}} O.\ (g) \longrightarrow H.\ (g)\ +\ :O\ (g) \quad \Delta H^0 = + \text{yJ}$$

Energy required to break O—H (1) and O—H (2) bonds, are different because bond breaking process for O—H (1) takes place in neutral H_2O molecule whereas bond breaking process for O—H (2) takes place in free radical (.OH).

Thus,

Bond dissociation enthalpy of O—H (1) $= +$ xJ.mole^{-1}

Bond dissociation enthalpy of O—H (2) $= +$ yJ.mole^{-1}

$$\therefore \textit{Bond enthalpy of O—H bond } = \frac{+x+y}{2} \textit{ J. mole}^{-1}$$

$$= +\frac{1}{2}(x+y)\textit{ J. mole}^{-1}$$

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