## THERMODYNAMICS

**Topic: 2**

**Heat capacities, Specific Heats, exothermic and endothermic processes, Enthalpy of bond dissociation, combustion, neutralization, formation, atomization, sublimation, phase transition, ionization and dilution.**

## VERY SHORT ANSWER QUESTIONS

**1. Explain enthalpy?**

**Enthalpy (H):** "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature"

Enthalpy is state function. Thus, the magnitude to enthalpy change depends only upon the enthalpies in the initial and final states.

$$\Delta H = [H_{products} - H_{reactants}]$$
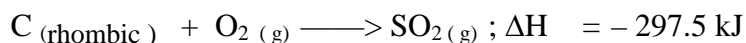
**2. What is heat capacity? Explain.**

**Ans. Heat capacity (C):** "Heat capacity of a substance is defined as the amount of heat required to raise its temperature through one degree"

Heat capacity (C) is a state function. Hence to evaluate 'C' the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

i)  Heat capacity at constant volume ($C_v$)

ii)  Heat capacity at constant pressure ($C_p$).

**3. What is thermo chemical equation? Give one example.**

**Ans: Thermo chemical equation:** The chemical equation in which heat change accompanying a reaction is also numerically specified with proper sign by $\Delta H$ (or) $\Delta E$ by the side of the equation are known as thermo chemical equation.

**Ex:** $C_{(graphite)} + O_{2\ (g)} \longrightarrow CO_{2\ (g)}$ ; $\Delta H = -393.5$ kJ

$C_{(rhombic)} + O_{2\ (g)} \longrightarrow SO_{2\ (g)}$ ; $\Delta H = -297.5$ kJ

## SHORT ANSWER QUESTIONS\

**2. State second law of thermodynamics.**

**Ans.  II law of thermodynamics:**

   **Statements:**

   i)  " It is impossible for a self acting machine unaided by any external agency to convert heat from a body at low temperature to a body at higher temperature".

   ii)   " All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes."

   iii)  "For any spontaneous process taking place in an isolated system, the change in entropy ($\Delta S$) is positive".

 **3. What is entropy?**

**Ans. Entropy:** is taken as a measure of disorder of molecules (or) randomness of system.
   Greater the disorder of molecules in a system, the higher is the entropy.
   Entropy is a state function. It depends on the temperature, pressure of the system.
   For a spontaneous process in an isolated system the entropy change is positive.

## LONG ANSWER QUESTIONS

**1. Give the criteria for spontaneity if it occurs on its own without intervention of any external agency of any kind.**

**Ans. Spontaneous reaction:**

A Process is said to be spontaneous if it occurs on its own without intervention of any external agency of any kind.

All natural processes are spontaneous.

Entropy increases in all spontaneous processes.

**Change in entropy "($\Delta S$)** = positive" is a condition but is not necessary and sufficient condition for the spontaneous nature of a reaction.

**Change in enthalpy "($\Delta H$) =** negative" may be a condition but not a necessary and sufficient condition for the spontaneous nature of a reaction.

At this juncture, "Gibbs" introduced another thermodynamic function which involves both enthalpy (H) and entropy (S) functions. This is known as free energy function (G). This is given by the equation, G = H – TS. 'G' is now referred as Gibbs energy' (or) Gibbs function.

$\Delta G_{sys}$ is negative "for spontaneous reactions (or) processes. Thus the spontaneity of a reaction and the algebraic signs of $\Delta H$, $\Delta S$, $\Delta G$ and the magnitude of 'T' can be related as follows:
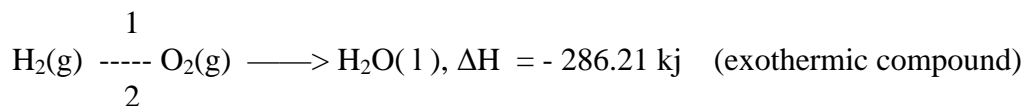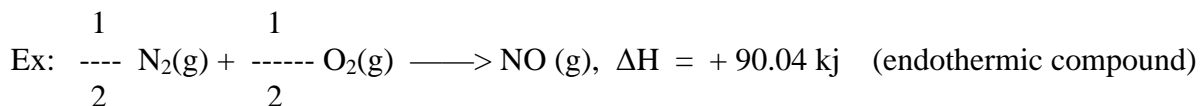
| $\Delta H$ | $\Delta S$ | $\Delta G$ | Nature of the reaction |
|:---:|:---:|:---:|:---|
| - | + | - | Spontaneous at all 'T' values. |
| + | - | + | Non - Spontaneous at all 'T' values. |
| - | - | - | Spontaneous at low 'T' values. |
| - | - | + | Non - Spontaneous at high 'T' values. |
| + | + | + | Non - Spontaneous at low 'T' values. |
| + | + | - | Spontaneous at high 'T' values. |

**3. Explain the terms with examples.**
**i)Heat of formation, ii) Heat of combustion and iii) Heat of solution.**

**Ans. i) Heat of formation ($\Delta H_f$):**

**Definition:** The amount of heat evolved (or) absoubed during the formation of one mole of the compound at constant temperature from the constituent elements in the standard state is heat formation.

Ex: $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO (g)$, $\Delta H = + 90.04$ kj   (endothermic compound)

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$, $\Delta H = - 286.21$ kj   (exothermic compound)
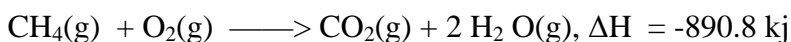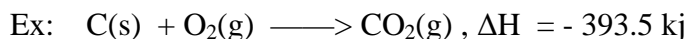
Compounds which liberate heat in their formation reaction from the constituent elements are called exothermic compounds. For this reactions, $\Delta H_f$ = (-) ve

Compounds which absorb heat in the formation reaction from the constituent elements are called endothermic compounds. For this reactions, $\Delta H_f$ = (+) ve

**ii) Heat of combustion**:

**Definition:** The heat evolved when one mole of a substance is completely burnt at constant volume in excess of oxygen.

Ex:   $C(s) + O_2(g) \longrightarrow CO_2(g)$ , $\Delta H$ = - 393.5 kj

$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + 2 H_2 O(g)$, $\Delta H$ = -890.8 kj

Combustion is a process of burning a chemical compound at high temperatures in presence of excess of $O_2$ (or) air at constant volume and at high pressures.

Combustion process is always an exothermic process.( $\Delta H$ = -ve)
**iii) Heat of solution:** The amount of heat evolved (or) absorbed when 1 mole of a solute is dissolved completely in large excess of solvent is called heat of solution.
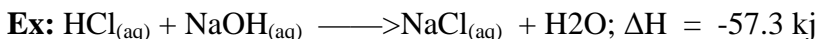
(or)

The change of enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to another.
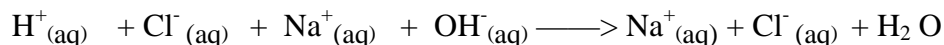
Ex:  $Kcl (s) + aq \longrightarrow Kcl(aq)$, $\Delta H$ = +19.75 kj
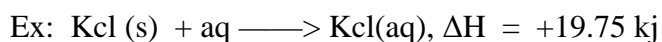
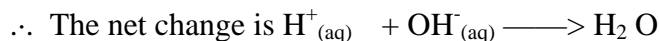This is measured per mole of solute. If solvent is water then it is called enthalpy of dilution.

**4. What is the heat of neutralization? How does its value change with the chemical nature of the acid and base: Give examples?**

**Ans. Heat of neutralization:** The amount of heat evolved when a gram - equivalent of an acid reacts with a gram equivalent of a base to form salt and water is called Heat of neutralization.
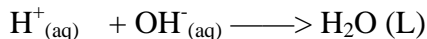
**Ex:** $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H2O$; $\Delta H$ = -57.3 kj

The ionic form of the above reaction is

$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2 O$
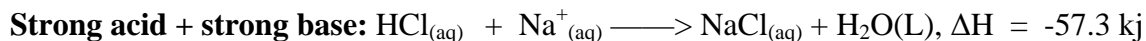
∴ The net change is $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O$

∴ The amount of heat evolved when 1 mole of water is formed from 1 mole $H^-$ ions is called Heat of neutralization.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O \text{ (L)}$$

Process is always exothermic. The amount of heat evolved depends on the chemical nature of the acid and the base.

**Strong acid + strong base:** $HCl_{(aq)} + Na^+_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(L)$, $\Delta H = -57.3$ kj
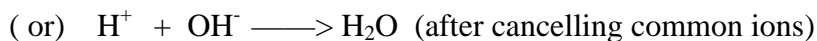
Heat of neutralization of a strong acid against strong base is always constant (-57.32 kj). It is because in dilute solutions all strong acids and bases ionise completely and thus heat of neutralization in such cases is actually the heat of formation of $H_2O$ from $H^+$ & $OH^-$ ions (i.e.,) $H^+ + OH^- \rightarrow H_2O$; $\Delta H = -57.32$kj.

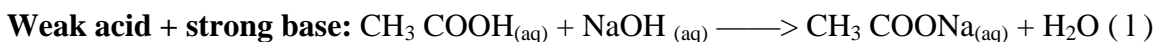**Strong acid + weak base:** $HCl_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O$; $\Delta H = -57.34$ kj

Heat of neutralization of weak base a against strong acid is always less than (-57.32 kj). Because apart of evolved heat is used up to ionise weak base ($NH_4OH$)

Heat of neutralization between $NH_4OH$ and HCl involves the following reactions:

a) $NH_4OH \xrightarrow{\ + H_2O\ } NH^+_4 + OH^-$, $\Delta H_1 = +5.98$ kj

b) $H^+ + Cl^- + NH^+_4 + OH^- \longrightarrow NH^+_4 + Cl^- + H_2O$, $\Delta H_2 = -57.32$ kj

( or) $H^+ + OH^- \longrightarrow H_2O$ (after cancelling common ions)

∴ The heat of neutralization of $NH_4OH + HCl$, $\Delta H = \Delta H_1 + \Delta H_2 = +5.98 + (57.32)$,

$$\Delta H = -51.34 \text{ kj}$$

**Weak acid + strong base:** $CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O \text{ ( l )}$
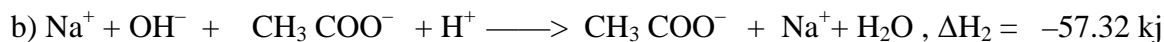
$$\Delta H = -55.23\text{kj}$$

Heat of neutralization of weak acid against strong base is always less than $-57.32$ kj because of a part of heat evolved is used up to ionise weak acid ($CH_3COOH$).

Heat of neutralization between $CH_3COOH$ and NaOH involves the following reactions.

a) $CH_3\ COOH\ \xrightarrow{+ H_2O}\ CH_3\ COO^- + H^+,\ \ \Delta H_1\ +\ 2.09kj$

b) $Na^+ + OH^- +\ CH_3\ COO^- + H^+ \longrightarrow CH_3\ COO^- + Na^+ + H_2O,\ \Delta H_2 =\ -57.32\ kj$

(or ) $OH^- + H^+ \longrightarrow H_2O$ (cancelling the common ions)

$\therefore$ The heat of neutralization of $CH_3COOH +\ NaOH,\ \Delta H =\ \Delta H_1 +\ \Delta H_2 =\ +\ 2.09 - 57.32;$

$$=\ 55.23kj$$

**Weak acid + weak base:**

$CH_3COOH_{(aq)}\ +\ NH_4OH\ _{(aq)}\ \longrightarrow CH_3\ COON\ H_{4\ (aq)}\ + H_2O$

$\Delta H = -49.25kj$. Heat of neutralization of weak acid against weak base is always less than $-57.32$ kj because of a part of heat evolved is used up to ionise weak acid $(CH_3COOH)$.and weak base $(NH_4OH)$

Heat of neutralization between $CH_3COOH$ and $NH_4OH$ involves the following reactions:

a) $CH_3\ COOH\ \xrightarrow{H_2O}\ CH_3\ COO^- + H^+,\ \ \Delta H_1\ +\ 2.09kj$

b) $NH_4OH\ \xrightarrow{+ H_2O}\ +\ NH^+_4\ , + OH^-\ \ \ \Delta H_2 =\ +\ 5.98kj$

c) $CH_3\ COO^- + H^+ + NH^+_4\ , + OH^-\ \longrightarrow CH_3\ COO^- + NH^+_4\ , + H_2O,\ \Delta H_3 =\ -57.32kj$
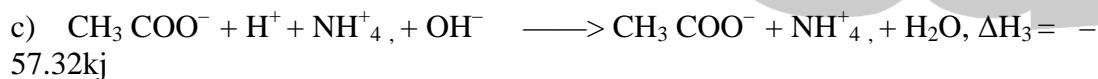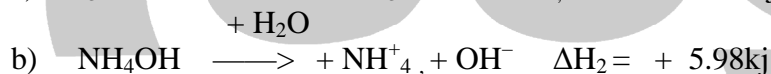
( or ) $H^+\ + OH^-\ \longrightarrow H_2O$ (after cancelling the common ions)

$\therefore$ Heat of neutralization of $CH_3\ COOH\ +\ NH_4OH,\ \Delta H =\ \Delta H_1 +\ \Delta H_2 +\ \Delta H_3$

$$=\ +\ 2.09 +\ 5.98 - 57.32;\ \Delta H = -49.25\ kj$$